Contents lists available at ScienceDirect

Dyes and Pigments

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

Efficient and stable deep-blue narrow-spectrum electroluminescence based on hybridized local and charge-transfer (HLCT) state

Shengbing Xiao^a, Shi-Tong Zhang^{a,**}, Ying Gao^a, Xinqi Yang^a, Haichao Liu^a, Weijun Li^b, Bing Yang^{a,*}

^a State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun, China ^b State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, China

ARTICLE INFO

Keywords: Phenanthroimidazole-acridine derivatives HLCT Deep-blue OLED

ABSTRACT

Two phenanthroimidazole-acridine derivatives (**DPM** and **TDPM**) were designed and synthesized for deep-blue organic light-emitting diode (OLED). Twisted combined rigid structures with hybridized local and charge-transfer (HLCT) state properties enable them to achieve excellent OLED performance. Non-doped OLEDs based on **DPM** and **TDPM** show decent deep-blue narrow-spectrum emission with Commission International de L'Éclairage (CIE) coordinates of (0.157, 0.053) and (0.158, 0.045), as well as maximum external quantum efficiency (EQE_{max}) of 4.0% and 2.6%, respectively. More importantly, OLEDs based on **TDPM** exhibit a smaller efficiency roll-off (12%) than that of **DPM** (35%) at high brightness (820 cd m⁻² for DPM and 893 cd m⁻² for TDPM, respectively). Overall, our work provides a molecular design strategy of HLCT materials for efficient deep-blue OLED with high color purity using purely organic emitter.

1. Introduction

Organic light-emitting diode (OLED) has attracted much attention for its potential commercial application in flat-panel display and solidstate lighting [1-4]. Over the past few years, great efforts have been made to improve OLED efficiency and stability through the exploration on new material systems and the optimization of device structures [5-9]. In the past two decades, the green- and red-emissive phosphorescent materials have been developed and commercialized very well [10-12]. However, despite that there have been many reports on the blue electro-phosphorescent OLED (PhOLED), efficient deep-blue phO-LEDs are still rare compared with blue and sky-blue phOLEDs [13,14]. Additionally, noble-metals are essential to the current organometallic complexes phosphors, which are potential pollutants and expensive. Therefore, the cheap and eco-friendly pure organic molecules are more promising to be the next-generation OLED materials, and it is necessary to explore the molecular design methods based on the structure-property relationship of them, especially the high-performance blue-emissive materials.

There are two key issues to be addressed for the ideal next-generation

blue electro-fluorescent materials: electro-exciton utilization and color purity [15]. On one hand, the most crucial drawback of the pure organic electro-fluorescent materials is that they can only utilize 25% of the total electro-exciton (that is, the singlet electro-exciton) in OLED due to the spin-statistics rule [16]. In recent years, some novel solutions have been proposed to the above electro-triplet utilization problem in pure organic electro-fluorescent materials, such as triplet-triplet annihilation (TTA) [17-19], the thermally activated delayed fluorescence (TADF) [20-23] and the hybridized local and charge-transfer (HLCT) state [24-26]. These materials can convert the electro-triplet excitons into the spin-transition-allowed singlet excitons in different paths, and achieve far better electroluminescence (EL) performance than the traditional fluorescent materials. Among these mechanisms, despite that some anthracene and pyrene derivatives have already been commercialized for the replacement of phosphorescent materials, the upper limit of exciton utilization efficiency (EUE) such TTA materials are only 62.5%, which is obviously not an ideal solution [27]. Besides, although the TADF OLEDs can harvest up to 100% electro-exciton through reverse intersystem crossing (RISC) of $T_1 \rightarrow S_1$, they often suffer a serious efficiency roll-off at high current density due to the inefficient RISC

https://doi.org/10.1016/j.dyepig.2021.109482





^{*} Corresponding author.

^{**} Corresponding author. E-mail addresses: stzhang@jlu.edu.cn (S.-T. Zhang), yangbing@jlu.edu.cn (B. Yang).

Received 11 March 2021; Received in revised form 11 May 2021; Accepted 11 May 2021 Available online 27 May 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.



Scheme 1. Previous work and our work.

processes and accumulated of T1 excitons. An effective method to deal with problem is to apply such TADF materials as an assistant host, passing on energy to the emitters through a Förster resonance energy transfer (FRET) process [28,29]. Therefore, the application of TADF materials in OLED relies heavily on the doping technology, which increases the cost and may hinder the successful commercialization to some extent. The HLCT state is a linear combination of excited state with a certain proportion between locally-excited (LE) state and charge-transfer (CT) excited state, corresponding to high photoluminescent (PL) efficiency and high EUE, respectively [30,31]. Different from TADF mechanism, HLCT materials can realize a high-efficiency electroluminescence from the fast RISC process along high-lying excited state channels ($T_m \rightarrow S_n$), demonstrating as no delayed component in the time-resolved PL measurement [32]. Meantime, the fast RISC can effectively suppress the accumulation of electro-triplet exciton and improve the stability of OLED at high voltage, which enables the practical application owing to the easy processing of non-doped OLED.

On the other hand, the color purity is also a very important index for the blue-emissive materials, since the good color purity of emitters have the optimal color-gamut and avoid unnecessary energy loss from the additional light filter in full-color display. Although TADF materials have successfully solved the spin-statics rule problem, the strong CT excited states usually lead to poor color purity due to the broad PL spectra [33,34]. More recently, a new class of boron- and nitrogen-containing heterocyclic TADF materials are reported with decent color purity, as a result of a well suppressed vibronic coupling by the so-called multi-resonance mechanism [35–37]. Nevertheless, their synthesis, especially the scale-up synthesis are still a very difficult task. Overall, HLCT state is still an effective strategy to realize blue-emission with good color purity, since the linear combination of LE excited state can reduce the spectral broadening of pure CT excited state to a certain degree.

Phenanthroimidazole (PM) group have been widely used to construct blue-emissive materials, because of its bipolar transport capability, high photoluminescence quantum yields (PLQY) and good thermal stability [39,40]. The earliest and the most representative works on the PM-based HLCT blue-emissive materials are a series of highly efficient triphenylamine (TPA)-substituted PM derivatives, such as TPA-PPI, TBPMCN [41,42]. However, their planar D-A configuration with large π -conjugated characteristics make it difficult for them to achieve a deep-blue emission, and non-doped OLEDs based on them both exhibit pure blue emission with CIE_y > 0.1. Meanwhile, their full width at half-maximum (FWHM) are still too large (about 75 nm), which

are far from the ideal one of <50 nm (Scheme 1). Therefore, it is necessary to develop efficient deep-blue OLEDs based on PM derivatives with reasonable molecular design.

In order to obtain efficient deep-blue emission materials with narrow FWHMs, appropriate CT components in HLCT state should be finely controlled in molecular design, together with a rigid donor unit to suppress molecular vibrations for both increased PLQY and narrow spectra. In this work, we synthesize two compounds: 2-2-(4-(9,9-dimethylacridin-10-(9H)-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (DPM) and 1-4-(tert-butyl)phenyl)-2-(4-(9,9-dimethylacridin-10 (9H)-yl)phenyl)-1H-phenanthro-[9,10-d]imi-dazole (TDPM), in which the planar and rigid function group 9,9-dimethyl-9,10-dihydroacridine (DMAC) serves as electron donor (D) and the PM moiety acts as electron acceptor (A). Compared with non-rigid donor (TPA), rigid donor (DMAC) could efficient suppress the molecular vibrations and rotations, which is beneficial to construct efficient deep-blue lighting materials. Tertbutyl (ttBu) is also introduced as a chemical modification to inhibit the aggregation caused quenching (ACQ) and improve emission color relative to the counterpart. As expected, both two materials display decent deep-blue emission with narrower FWHMs compared with TPAsubstituted PM derivatives. Non-doped OLEDs based on DPM and TDPM share maximum external quantum efficiency (EQE) of 4.0% and 2.6% with CIE coordinates of (0.157, 0.053) and (0.158, 0.045) and low efficiency roll-off of 35% and 12% at high brightness (820 cd m^{-2} for DPM and 893 cd m^{-2} for **TDPM**), as well as narrow FWHMs of 52 nm and 49 nm, respectively.

2. Experimental section

2.1. General information

¹H NMR and ¹³C NMR were recorded on a Bruker AVANCZ 500 spectrometer at 500 MHz using deuterated dimethyl sulfoxide (DMSO) as the solvent for ¹H NMR and CDCl₃ as the solvent for ¹³C NMR at 298 K. Tetramethylsilane (TMS) was used as internal standards. The MALDI-TOF mass spectra were recorded by an AXIMA-CFRTM plus instrument. The Flash EA 1112, CHNS–O elemental analysis instrument was chosen to characterize these compounds. Diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K α and control Software using the RAPID AUTO at 293 (±2) K. The differential scanning calorimetry (DSC, DSC Q100) PerkinElmer thermal analysis system was set at a heating rate of 10 °C min⁻¹ and a nitrogen flow rate of 50 mL min⁻¹. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analysis system from 30 °C to



Scheme 2. Synthesis route of DPM and TDPM.

800 °C with a heating rate of 10 °C min⁻¹. UV–vis absorption spectra and Fluorescence spectra were recorded by the UV-3100 spectrophotometer and RF-5301PC, respectively. Corrected PLQY is obtained by manual operation using an integrating sphere apparatus. Transient photoluminance decay characteristics were measured using an Edinburgh Instruments F980 spectrometer. Cyclic voltammetry (CV) was carried out using BAS 100B/W electrochemical analyzer with standard one-compartment, three-electrode electrochemical cell. A glass-carbon disk electrode was selected as a working electrode. Pt wire was performed as a counter electrode. Ag/Ag⁺ was used as a reference electrode with Ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal standard.

2.2. Device fabrication and performances

ITO-coated glass was used as the substrate with a sheet resistance of 20 Ω square⁻¹. The ITO glass was cleaned by ultrasonic cleaner with deionized water, isopropyl alcohol, acetone and chloroform. The evaporation rate was controlled to be 0.03–0.1 nm/s for organic layers, 0.01 nm s⁻¹ for the LiF layer was and 0.3 nm/s for the Al layer. The PR650 spectra scan spectrometer was used to record EL spectrum and luminance-current density-voltage was measured by spectrometer with a Keithley model 2400 programmable voltage-current source. Evaporated films were also produced under same conditions.

2.3. Synthetic procedures

All reagents and solvents were purchased from commercial source and used directly unless otherwise specified. All reactions were performed under nitrogen atmosphere. Column chromatography was performed using silica gel (200–300). Detail synthesis route is shown in Scheme 2.

2.3.1. PM-Br

A mixture of 9,10-phenanthrenequinone (4.16 g, 20 mmol), aniline (7.4 mL, 80 mmol), 4-Bromobenzaldehyde (3.70 g, 20 mmol) ammonium acetate (7.7 g, 100 mmol), acetic acid (50 mL) was heated to 120 °C, and stirred for 4 h under nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to give a yellow solid and washed with a small amount of acetic acid and water, then dried under vacuum. Crude products were purified by column chromatography to obtain a white solid. (7.71 g, yield = 86%). (eluent: dichloromethane (CH₂Cl₂)). The products were not further purified and directly used for the next reaction. MS:MW 448.06, m/z = 447.84 (M⁺). ¹H NMR (500 MHz, DMSO) δ 8.94 (d, J = 8.3 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.69 (dd, J = 7.9, 1.1 Hz, 1H), 7.78 (q, J = 6.9 Hz, 1H), 7.76–7.68 (m, 6H), 7.61–7.54 (m, 3H), 7.54–7.48 (m, 2H), 7.35 (dd, J = 11.3, 4.1 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H).

2.3.2. TPM-Br

A mixture of 9,10-phenanthrenequinone (4.16 g, 20 mmol), 4-tertbutylanilineaniline (12.80 mL, 80 mmol), 4-Bromobenzaldehyde (3.70 g, 20 mmol) ammonium acetate (7.7 g, 100 mmol), acetic acid (50 mL) was heated to 120 °C, and stirred for 4 h under nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to give a yellow solid and washed with a small amount of acetic acid and water, then dried under vacuum. Crude products were purified by column chromategraphy using to obtain a white solid (7.42 g, yield = 74%). Eeluent: CH₂Cl₂. Crude products were used directly used for the next reaction. MS:MW 504.06, m/z = 504.12. (M⁺).¹H NMR (500 MHz, DMSO) δ 8.93 (d, J = 8.2 Hz, 1H), 8.88 (d, J = 8.4 Hz, 1H), 8.69 (d, J =7.9 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.74–7.66 (m, 3H), 7.63 (d, J = 8.4Hz, 2H), 7.57 (dd, J = 12.0, 5.2 Hz, 3H), 7.51 (d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 7.7 Hz, 1H), 1.42 (s, 9H).

2.3.3. DPM

A mixture of PM-Br (1.48 g, 3.3 mmol), 9,9-dimethyl-9,10-dihydroacridine (627 mg, 3.0 mmol), sodium tert-butoxide (t-BuONa; 2.24 g, 20 mmol), tri-tert-butylphosphine solution ($P(t-Bu)_3$; 1.0 mL, 0.86 g), tris (dibenzylideneacetone)dipalladium (Pd2(dba)3, (120 mg)) was dissolved in dry toluene (30 mL), and purged three times by nitrogen/ vacuum cycle. Then the reaction was heated to 110 °C and refluxed for 36 h. After cooling to room temperature, the mixture was washed with 20 mL water and extracted with CH₂Cl₂ for several times. The organic phase was dried over sodium sulfate (Na₂SO₄). The products were purified by chromatography using the mixture of CH₂Cl₂: petroleum ether 1:2 as eluent to give a white solid. The products were further purified by sublimation. (1.45 g, yield = 84%). MS:MW 577.22, m/z = 576.87. (M⁺). ¹H NMR (500 MHz, DMSO) δ 8.97 (d, J = 8.4 Hz, 1H), 8.92 (d, J =8.4 Hz, 1H), 8.74 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 11.3, 3.7 Hz, 3H), 7.77–7.69 (m, 4H), 7.59 (t, J = 7.2 Hz, 1H), 7.50 (dd, J = 7.7, 1.4 Hz, 2H), 7.38 (t, J = 7.8 Hz, 3H), 7.15 (d, J = 7.7 Hz, 1H), 7.04–6.96 (m, 2H), 6.95–6.89 (m, 2H), 6.12 (dd, J = 8.2, 1.0 Hz, 2H), 1.62 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 150.11 (s), 141.76 (s), 140.71 (s), 138.70 (s), 137.58 (s), 131.86 (s), 131.28 (s), 130.50-129.77 (m), 129.15 (s), 127.34 (d, J = 24.3 Hz), 126.40 (s), 125.84 (s), 125.21 (d, J = 15.7 Hz), 124.23 (s), 123.25 (s), 123.24–123.13 (m), 122.95 (d, J = 25.4 Hz), 120.88 (d, J = 21.8 Hz), 120.77–120.49 (m), 114.14 (s), 77.21 (dd, J = 54.7, 22.8 Hz), 36.05 (d, J = 6.5 Hz), 31.22 (d, J = 7.4 Hz), 29.77 (s). Element Analysis: Calculate for C42H31N3: C, 87.32; H, 5.41; N,7.27; Found: C, 88.08; H, 5.26; N, 7.32.

2.3.4. TDPM

A mixture of TPM-Br (1.66 g, 3.3 mmol), 9,9-dimethyl-9,10-dihydroacridine (627 mg, 3.0 mmol), *t*-BuONa (2.24 g, 20 mmol), $P(t-Bu)_3$ (1.0 mL, 0.86 g), $Pd_2(dba)_3$ (120 mg) was dissolved in dry toluene (30 mL), and purged three times by nitrogen/vacuum cycle. Then the reaction was heated to 110 °C and refluxed for 36 h. After cooling to room temperature, the mixture was washed with 20 mL water and extracted



Fig. 1. (a) Molecular geometries (b) The S1 NTOs of DPM and TDPM, respectively. f: oscillator strength.

with CH_2Cl_2 for several times. The organic phase was dried over Na_2SO_4 . The crude products were purified by chromatography using the mixture of CH_2Cl_2 : petroleum ether 3:4 as eluent to give a white solid. The products were further purified by sublimation. (1.22 g, yield = 64%). MS:MW 633.12, m/z = 633.13. (M⁺). ¹H NMR (500 MHz, DMSO) δ 8.96 (d, J = 8.5 Hz, 1H), 8.91 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 6.8 Hz, 1H),



Fig. 2. Photophysical properties of DPM and TDPM in different solutions. (a) Normalized UV absorption spectra. (b) Normalized PL spectra. (c) Lippert-Mataga models (d) Normalized transient PL spectra. All measurements were performed in solutions $(1*10^{-5} \text{ M})$ at room temperature.



Fig. 3. Thermal properties. (a) Thermal gravimetric analysis (TGA), T_d: decomposition temperatures (5% weight loss). (b) Differential scanning calorimetry (DSC), T_g: glass transition temperatures.

7.86 (d, J = 8.4 Hz, 2H), 7.81 (t, J = 7.5 Hz, 1H), 7.76–7.67 (m, 5H), 7.59 (t, J = 7.7 Hz, 1H), 7.50 (dd, J = 7.6, 1.5 Hz, 2H), 7.37 (dd, J = 15.2, 7.9 Hz, 3H), 7.21 (d, J = 8.2 Hz, 1H), 7.02–6.87 (m, 4H), 6.10 (dd, J = 8.1, 1.2 Hz, 2H), 1.62 (s, 6H), 1.41 (s, 9H). 13C NMR (126 MHz, CDCl3) δ 153.55 (s), 150.34 (s), 141.62 (s), 140.74 (s), 137.48 (s), 135.88 (s), 131.88 (s), 131.18 (s), 130.69 (s), 130.14 (s), 129.42 (s), 128.50 (d, J = 19.9 Hz), 127.47 (s), 127.46–126.80 (m), 126.40 (s), 125.59 (d, J = 46.6 Hz), 125.20 (d, J = 25.9 Hz), 125.00–124.71 (m), 124.19 (s), 123.21 (d, J = 9.0 Hz), 123.01 (d, J = 39.8 Hz), 121.04 (s), 130.79 (s), 114.11 (s), 77.41 (s), 77.16 (s), 76.90 (s), 36.05 (s), 35.11 (s), 31.38 (d, J = 26.3 Hz), 31.21–30.89 (m). Element Analysis: Calculate for C4₆H₃₉N₃: C, 87.17; H, 6.20; N,6.63; Found: C, 87.64; H, 6.17; N, 6.57.

3. Results and discussion

3.1. Theoretical calculations

To deeply understand the molecular design, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at M062X/6-31g (d, p) level were carried out to calculate electronic structures using Gaussian 09 D.01 package [44-46]. As shown in Fig. S1, the close energy level of the highest occupied molecular orbital (HOMO) between DMAC and PM (or TPM) can avoid the formation of strong intramolecular CT excited state, and maintain a high PLQY. The optimized molecular geometries (Fig. 1a) show that the D-A twist angle of the two molecules are both near 90°. The side group (phenyl or 4-tert-butylphenyl) and imidazole ring also display large dihedral angles of 71° and 73° for DPM and TDPM, respectively. This largely twisted structure of DPM and TDPM can prevent the formation of excimer and exciplex species, leading to the emission quenching and color-impurities. Moreover, the largely twisted D-A structures also bring about the separation of HOMO and LUMO distributions (Fig. S2). The HOMO and LUMO are mainly located on the DMAC and PM units, respectively. Furthermore, we characterized their electrochemical properties by cyclic voltammetry (CV) method (Fig. S3). According to the CV analysis, the HOMO energy levels of DPM and TDPM are calculated to be -5.39 eV and -5.16 eV VS ferrocene. The LUMO energy levels are calculated to be -2.44 eV and -2.53 eV. Consistent with the theoretical results, it shows that the two materials both have decent capability of carrier injection. The natural transition orbitals (NTOs) of the S1 excited state also demonstrate their CT-dominated excited state characters (Fig. 1b).

3.2. Photophysical properties

From above theoretical calculations, tBu-substitution does not make any difference on the electron transition essence of excited state in these two materials. We then carried out photophysical characterizations on them for the purpose of comparison. Firstly, both ultraviolet–visible

(UV) absorption and PL spectra of these two materials were measured in diluted solutions with different solvent polarities at room temperature. Consistent with the theoretical results, they share very similar photophysical properties. As shown in Fig. 2a, DPM and TDPM display a similar absorption behavior, and their strong absorption band around 260 nm originates from the π - π * transition of the isolated benzene ring attached to the nitrogen of imidazole [10,47]. The medium absorption band around 280–350 nm can be assigned to the π - π * transition of the PM and TPM moieties. The weak absorption band at 365 nm can be assigned to the intramolecular CT transition. Interestingly, the vibronic structures disappear with the increase of solvent polarity, and the obvious CT spectral characteristics (smooth and broadened PL, large solvatochromic redshift) can be observed in high-polarity solvents such as tetrahydrofuran (THF) and acetonitrile, while their PL spectra both exhibit LE state character with vibronic structures in the low-polarity solvent hexane (Fig. 2b). Lippert-Mataga model of these two materials both demonstrate clear linear relation between Stokes shift and solvent polarity factor f, reflecting a quasi-equivalent HLCT excited states from both LE and CT excited states (Fig. 2c). Furthermore, the dipole moment (μ_e) of S₁ excited state of these two materials can be estimated as 14.7 D and 14.8 D, respectively, which are relative moderate values comparing to those of traditional strong CT materials, indicating that the large twist structure will not significantly affect the PLQY and color-purity. Lifetime measurements also confirm the HLCT character of these two materials: the nanosecond-scale single exponential decay and the gradually extended lifetime with increasing solvent polarity (Fig. 2d). In addition, the energy gap (ΔE_{ST}) between S₁ and T₁ were calculated to be 0.56 eV and 0.59 eV according to their fluorescence emission peaks and phosphorescent emission peaks (Fig. S5). Therefore, TADF mechanism with reverse intersystem crossing (RISC) process from T₁ to S₁ seems to be impossible in these two materials. Besides, we also do not observe the long lifetime from transient PL spectra of their evaporated film in air at room temperature. (Fig. S6). In short, twisted and rigid structures, appropriate CT components, and bulk t-Bu substitution make the two materials display a deep-blue emission, narrow FWHM and high PLQY [48-50].

3.3. Thermal stabilities

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to investigate the thermal stability of **DPM** and **TDPM** under nitrogen atmosphere (Fig. 3). Both of them demonstrate high thermal stability owing to the rigid structures. The decomposition temperatures of these two materials (T_d, 5% weight loss) are 437 °C for DPM and 433 °C for TDPM, respectively. What is more, they also exhibit glass transition temperatures (T_g) as high as 134 °C and 133 °C respectively, which are beyond the 120 °C criterion of OLED industrial application [12].

Table 1

Non-doped OLED performances of DPM and TDPM.

Emitter	$V_{on}^{1}(V)$	$\lambda_{\rm EL}^2$ (nm)	CE_{max}^{3} (cd/A)	PE _{max4} (lm/w)	$CIE^{5}(x, y)$	EQE ⁶ (%)	FWHM ⁷ (nm)	EUE ⁸ (%)
DPM	3.1	428	1.77	1.39	(0.157,0.053)	4.0	52	61
TDPM	3.1	424	0.99	0.95	(0.158,0.045)	2.6	49	65

 V_{on}^1 : Opening voltage at the brightness of 1 cd m⁻²; λ_{max}^2 : EL peak at the voltage of 6 V; CE_{max}^3 : Maximum current efficiency; PE_{max}^4 : Maximum power efficiency. CIE⁵ (x, y) at the voltage of 5 V. EQE⁶: Maximum external quantum efficiency; FWHM⁷: Full-width at half-maximum. EUE⁸: exciton utilization efficiency.



Fig. 4. OLED structures and key performances. (a) Energy level diagram of device structures. (b) (c) EL spectra at different voltages. (d) Current density-voltageluminance characteristics. (d) Current efficiency-luminance-power efficiency characteristics. (e) EQE versus luminance plots.

3.3.1. OLED performances

Considering the decent deep-blue emission in evaporated films and high thermal stability of these two materials, their non-doped bottomemitting OLEDs have been fabricated with the structure of the structure of ITO/HATCN (5 nm)/TAPC (20 nm)/TCTA (10 nm)/emitting layer (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm) (DPM) and ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (10 nm)/emitting layer (20 nm)/TPBI (35 nm)/LiF (1 nm)/Al (100 nm) (TDPM). Benefiting from their HLCT excited state, both these two materials achieve efficient and stable electro-fluorescence emission in OLED (Fig. 4Table 1). Both EL of DPM and TDPM exhibit stable deep-blue emissions of 428 nm and 424 nm, corresponding to the CIE of (0.157, 0.053) and (0.158, 0.045) respectively, which are in good agreement with their evaporated films. (Fig. S6). It is noteworthy that their FWHMs were effectively narrowed (~50 nm) compared with those of the PM-based HLCT blue-emissive materials in the previous works, especially in terms of the CIE y-coordinate. In addition, DPM and TDPM OLEDs show low turn-on voltages of about 3.1 V, maximum EQEs of 4.0% and 2.6%, respectively. Especially, the efficiency roll-off of TDPM is only 13% at the brightness of 892 cd m⁻², which indicates OLEDs based on **TDPM** display excellent OLED stability. More importantly, based on the above OLED structures, the thickness of emitter layers appears to have little effect on the EL spectrum and efficiency as shown in Fig. S7 and Fig. S8.

Furthermore, the EUE of OLEDs were estimated according to the equation as below:

$$EQE = (\gamma \times EUE \times \Phi_{PL}) \times \eta_{out}$$

where γ is the recombination efficiency of the injected electron and hole (generally identified as 100%); ϕ_{PL} is the PLQY of the emitter; η_{out} is the

light out-coupling fraction, which is estimated as ~ 20% for the glass substrates [51]. For **DPM** and **TDPM**, the EUEs are calculated to be 61% and 65% respectively, which both break through the upper limit 25% of spin statistics. The exceeding EUE of these two materials can be understood from their excited state energy levels and NTOs (Fig. 5). On one hand, although the energy gaps (ΔE_{ST}) between S₁ and T₁ are too large for conventional TADF mechanism, their S₁ and T₅ energy gaps are small enough (0.01eV for **DPM** and 0.04eV for **TDPM**, respectively) to afford efficient RISC. On the other hand, the NTOs of S₁ and T₅ are of similar HLCT transition character, which is in accordance with the "hot exciton" mechanism between high-lying excited states (T_m→S_n) [52].

The last but not the least, tBu substitution usually induces an increase of PLQY and EQE in OLED devices. However, the PLQY of TDPM is only 20% comparing to the 33% of **DPM** in evaporated films (Fig. S6), which directly brings down its OLED performance. We then prepared their single crystals to clarify this issue by investigating their structural differences and intermolecular interactions (Fig. 6). Similar to their optimized geometries, both conformations of DPM and TDPM display large D-A twist, as well as the dihedral angle between the side group (phenyl or 4-tert-butylphenyl) and imidazole ring in single crystals. However, their intermolecular interactions are quite different. The tBu in TDPM produces an extra C-H··· π interactions between the 4-tert-butylphenyl side group and the PM π -plane of an adjacent **TDPM** molecule, which also causes obvious long-range ordered π - π stacking of PM moieties that can affect the PLQY (31% for DPM crystal and 19% for TDPM crystal). In fact, the non-radiative transition rate (k_{nr}) of **TDPM** is 0.84 times that of **DPM** crystal, while the radiative transition rate (k_r) of **TDPM** is only 0.43 times that in DPM crystal, indicating that H-aggregation results in the fluorescence quenching in a certain degree (Fig. S10, Table S3).



Fig. 5. Excited state energy diagram and NTOs of S₁, T₁ and T₅ for DPM (a, b) and TDPM (c, d), respectively. f: oscillator strength.



Fig. 6. Crystal structures and the main intermolecular interactions of DPM (a) and TDPM (b), respectively. (Crystal DPM was obtained by slow volatilization of dichloromethane and methanol with a volume of 2:1 (c $< 10^{-5}$ mol/L), and the single crystal of TDPM was prepared by sublimation at the temperature of 270–280 °C under vacuum environment.).

More importantly, the *t*Bu induced extra C–H··· π interactions can surely optimize the efficiency roll-off in **TDPM**, which implies that *t*Bu substitution can be a potential strategy for the new-generation electro-fluorescent materials with nice color purity and stable electroluminescence.

4. Conclusion

In summary, two phenanthroimidazole-acridine derivatives DPM

and **TDPM** have been designed and synthesized for high-performance deep-blue OLEDs. Benefiting from the twisted and rigid structures with HLCT properties, non-doped OLEDs using **DPM** and **TDPM** as emitters achieve the excellent deep-blue emissions peaking at 428 nm and 424 nm, maximum EQEs of 4.0% and 2.6%, along with narrow FWHMs of 52 nm and 49 nm, respectively. Although the introduction of tBu leads a poorer PLQY and EQE, it can induce extra C-H… π interactions and ordered π - π stacking, which favors the EL stability than that of **DPM**. The *t*Bu substitution is still a promising strategy for the

molecule design to realize the efficient and stable electro-fluorescent materials with good color purity. Overall, our work is very helpful to design efficient deep-blue OLED in the future.

Author contribution statement

S. Xiao, Y. Gao, X. Yang performed the experiment and S. Xiao wrote the original manuscript.

H. Liu and W. L: Methodology, Formal analysis.

S. Zhang and B. Yang supervised the whole work and revised the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank the support from the National Natural Science Foundation of China (51803071, 91833304 and 51603185), the National Basic Research Program of China (2016YFB0401001), the Postdoctoral Innovation Talent Support Project (BX20180121), the China Postdoctoral Science Foundation (2018M641767), and JLUSTIRT (2019TD-33).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109482.

References

- Tang CW, VanSlyke SA. Organic electroluminescent diodes. Appl Phys Lett 1987; 51:913–5.
- [2] Zhu M, Yang C. Blue fluorescent emitters: design tactics and applications in organic light-emitting diodes. Chem Soc Rev 2013;42:4963–76.
- [3] Xu Y, Xu P, Hu D, Ma Y. Chem Soc Rev 2021;50:1030-69.
- [4] Wang M, Cheng Z, Meng X, Gao Y, Yang X, Liu H, Zhang S-T, Ma H, Yang B. Deep blue electro-fluorescence and highly efficient chemical warfare agent sensor: functional versatility of weak coupling hybridized locally excited and chargetransfer excited state. Dyes Pigments 2020;177:108317.
- [5] Wong MY, Zysman-Colman E. Purely organic thermally activated delayed fluorescence materials for organic light-emitting diodes. Adv Mater 2017;29: 1605444.
- [6] Maheshwaran A, Sree VG, Park H-Y, Kim H, Han SH, Lee JY, Jin S-H. High efficiency deep-blue phosphorescent organic light-emitting diodes with CIE x, y (≤ 0.15) and low efficiency roll-off by employing a high triplet energy bipolar host. Mater Adv Funct Mater 2018;28:1802945.
- [7] Wei Q, Fei N, Islam A, Lei T, Hong L, Peng R, Fan X, Chen L, Gao P, Ge Z. Small-molecule emitters with high quantum efficiency: mechanisms, structures, and applications in OLED devices. Adv Opt Mater 2018;6:1800512.
- [8] Xu Y, Liang X, Zhou X, Yuan P, Zhou J, Wang C, Li B, Hu D, Qiao X, Jiang X, Liu L, Su SJ, Ma D, Ma Y. Highly efficient blue fluorescent OLEDs based on upper level triplet-singlet intersystem crossing. Adv Mater 2019;31:1807388.
- [9] Tang X, Pan R, Zhao X, Jia W, Wang Y, Ma C, Tu L, Xiong Z. Full confinement of high-lying triplet states to achieve high-level reverse intersystem crossing in rubrene: a strategy for obtaining the record-high EQE of 16.1% with low efficiency roll-off. Adv Funct Mater 2020;30:2005765.
- [10] Huang Z, Wang B, Zhang Q, Xiang S, Lv X, Ma L, Yang B, Gao Y, Wang L. Highly twisted bipolar emitter for efficient nondoped deep-blue electroluminescence. Dyes Pigments 2017;140:328–36.
- [11] Lee J-H, Chen C-H, Lee P-H, Lin H-Y, Leung M-k, Chiu T-L, Lin C-F. Blue organic light-emitting diodes: current status, challenges, and future outlook. J Mater Chem C 2019;7:5874–88.
- [12] Lv X, Sun M, Xu L, Wang R, Zhou H, Pan Y, Zhang S, Sun Q, Xue S, Yang W. Highly efficient non-doped blue fluorescent OLEDs with low efficiency roll-off based on hybridized local and charge transfer excited state emitters. Chem Sci 2020;11: 5058–65.
- [13] Lee J, Chen H-F, Batagoda T, Coburn C, Djurovich PI, Thompson ME, Forrest SR. Deep blue phosphorescent organic light-emitting diodes with very high brightness and efficiency. Nat Mater 2015;15:92–8.
- [14] Im Y, Byun SY, Kim JH, Lee DR, Oh CS, Yook KS, Lee JY. Recent progress in highefficiency blue-light-emitting materials for organic light-emitting diodes. Adv Funct Mater 2017;27:1603007.

- [15] Zhang S-T, Bai X, Li X, Bai Q, Wang M, Liu H, et al. Assistant acceptor induced hybrid local and charge transfer blue-emissive electro-fluorescent materials based on locally excited triphenylamine-phenanthroimidazole backbone. Organic Electronics 2019;75:105404.
- [16] Segal M, Baldo MA, Holmes RJ, Forrest SR, Soos ZG. Excitonic singlet-triplet ratios in molecular and polymeric organic materials. Phys Rev B 2003;68. 075211.
- [17] Sinha S, Monkman AP. Delayed electroluminescence via triplet-triplet annihilation in light emitting diodes based on poly[2-methoxy-5-(2'-ethyl- hexyloxy)-1,4phenylene vinylene]. Appl Phys Lett 2003;82:4651–3.
- [18] Tang X, Bai Q, Shan T, Li J, Gao Y, Liu F, Liu H, Peng Q, Yang B, Li F, Lu P. Efficient nondoped blue fluorescent organic light-emitting diodes (OLEDs) with a high external quantum efficiency of 9.4% @ 1000 cd m-2 based on phenanthroimidazole-anthracene derivative. Adv Funct Mater 2018;28:1705813.
- [19] Xing L, Zhu Z-L, He J, Qiu Z, Yang Z, Lin D, et al. Anthracene-based fluorescent emitters toward superior-efficiency nondoped TTA-OLEDs with deep blue emission and low efficiency roll-off. Chem Eng J 2020:127748. https://doi.org/10.1016/j. cej.2020.127748.
- [20] Uoyama H, Goushi K, Shizu K, Nomura H, Adachi C. Highly efficient organic lightemitting diodes from delayed fluorescence. Nature 2012;492:234–8.
- [21] Yang S-Y, Wang Y-K, Peng C-C, Wu Z-G, Yuan S, Yu Y-J, et al. Circularly polarized thermally activated delayed fluorescence emitters in through-space charge transfer on asymmetric spiro skeletons. J Am Chem Soc 2020;142. 17756–11765.
- [22] Zhang D, Song X, Gillett AJ, Drummond BH, Jones STE, Li G, He H, Cai M, Credgington D, Duan L. Efficient and stable deep-blue fluorescent organic lightemitting diodes employing a sensitizer with fast triplet upconversion. Adv Mater 2020;32:1908355.
- [23] Liu H, Zeng J, Guo J, Nie H, Zhao Z, Tang BZ. High-performance non-doped OLEDs with nearly 100 % exciton use and negligible efficiency roll-off. Angew Chem Int Ed 2018;57:9290–4.
- [24] Chen L, Zhang S, Li H, Chen R, Jin L, Yuan K, Li H, Lu P, Yang B, Huang W. Breaking the efficiency limit of fluorescent OLEDs by hybridized local and chargetransfer host materials. J Phys Chem Lett 2018;9:5240–5.
- [25] Fu C, Luo S, Li Z, Ai X, Pang Z, Li C, Chen K, Zhou L, Li F, Huang Y, Lu Z. Highly efficient deep-blue OLEDs based on hybridized local and charge-transfer emitters bearing pyrene as the structural unit. Chem Commun 2019;55:6317–20.
- [26] Zhang H, Zhang B, Zhang Y, Xu Z, Wu H, Yin PA, Wang Z, Zhao Z, Ma D, Tang BZ. A multifunctional blue-emitting material designed via tuning distribution of hybridized excited-state for high-performance blue and host- sensitized OLEDs. Adv Funct Mater 2020;30:2002323.
- [27] Chiang C-J, Kimyonok A, Etherington MK, Griffiths GC, Jankus V, Turksoy F, Monkman AP. Ultrahigh efficiency fluorescent single and Bi-layer organic light emitting diodes: the key role of triplet fusion. Adv Funct Mater 2013;23:739–46.
- [28] Zhang D, Song X, Cai M, Duan L. Blocking energy-loss pathways for ideal fluorescent organic light-emitting diodes with thermally activated delayed fluorescent sensitizers. Adv Mater 2018;30:1705250.
- [29] Song X, Zhang D, Lu Y, Yin C, Duan L. Understanding and manipulating the interplay of wide-energy-gap host and TADF sensitizer in high-performance fluorescence OLEDs. Adv Mater 2019;31:1901923.
- [30] Li W, Pan Y, Yao L, Liu H, Zhang S, Wang C, Shen F, Lu P, Yang B, Ma Y. A hybridized local and charge-transfer excited state for highly efficient fluorescent OLEDs: molecular design, spectral character, and full exciton utilization. Adv Opt Mater 2014;2:892–901.
- [31] Gao Y, Zhang S, Pan Y, Yao L, Liu H, Guo Y, Gu Q, Yang B, Ma Y. Hybridization and de-hybridization between the locally-excited (LE) state and the charge-transfer (CT) state: a combined experimental and theoretical study. Phys Chem Chem Phys 2016;18:24176–84.
- [32] Xu Y, Xu P, Hu D, Ma Y. Recent progress in hot exciton materials for organic lightemitting diodes. Chem Soc Rev 2021;50:1030–69.
- [33] Chen WC, Yuan Y, Ni SF, Tong QX, Wong FL, Lee CS. Achieving efficient violet-blue electroluminescence with CIE y <0.06 and EQE >6% from naphthyl-linked phenanthroimidazole-carbazole hybrid fluorophores. Chem Sci 2017;8:3599–608.
- [34] Xu Y, Liang X, Liang Y, Guo X, Hanif M, Zhou J, Zhou X, Wang C, Yao J, Zhao R, Hu D, Qiao X, Ma D, Ma Y. Efficient deep-blue fluorescent OLEDs with a high exciton utilization efficiency from a fully twisted phenanthroimidazole-anthracene emitter. ACS Appl Mater Interfaces 2019;11:31139–46.
- [35] Hatakeyama T, Shiren K, Nakajima K, Nomura S, Nakatsuka S, Kinoshita K, Ni J, Ono Y, Ikuta T. Ultrapure blue thermally activated delayed fluorescence molecules: efficient HOMO-LUMO separation by the multiple resonance effect. Adv. Mater. 2016;28:2777–81.
- [36] Ahn DH, Kim SW, Lee H, Ko IJ, Karthik D, Lee JY, Kwon JH. Highly efficient blue thermally activated delayed fluorescence emitters based on symmetrical and rigid oxygen-bridged boron acceptors. Nat Photonics 2019;13:540–6.
- [37] Li X, Shi Y-Z, Wang K, Zhang M, Zheng C-J, Sun D-M, Dai G-L, Fan X-C, Wang D-Q, Liu W, Li Y-Q, Yu J, Ou X-M, Adachi C, Zhang X-H. Thermally activated delayed fluorescence carbonyl derivatives for organic light-emitting diodes with extremely narrow full width at half-maximum. ACS Appl Mater Interfaces 2019;11:13472–80.
- [39] Zhang Y, Wang J-H, Han G, Lu F, Tong Q-X. Phenanthroimidazole derivatives as emitters for non-doped deep-blue organic light emitting devices. RSC Adv 2016;6: 70800–9.
- [40] Yu Y, Zhao R, Liu H, Zhang S, Zhou C, Gao Y, Li W, Yang B. Highly efficient deepblue light-emitting material based on V-shaped donor-acceptor triphenylaminephenanthro[9,10-d]imidazole molecule. Dyes Pigments 2020;180:108511.
- [41] Li W, Liu D, Shen F, Ma D, Wang Z, Feng T, Xu Y, Yang B, Ma Y. A twisting donoracceptor molecule with an intercrossed excited state for highly efficient, deep-blue electroluminescence. Adv Funct Mater 2012;22:2797–803.

S. Xiao et al.

- [42] Zhang S, Yao L, Peng Q, Li W, Pan Y, Xiao R, Gao Y, Gu C, Wang Z, Lu P, Li F, Su S, Yang B, Ma Y. Achieving a significantly increased efficiency in nondoped pure blue fluorescent OLED: a quasi-equivalent hybridized excited state. Adv Funct Mater 2015;25:1755–62.
- [44] Lu T, Chen F. Multiwfn: a multifunctional wavefunction analyzer. J Comput Chem 2012;33:580–92.
- [45] Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor Chem Acc 2008;120: 215–41.
- [46] Martin RL. Natural transition orbitals. J Chem Phys 2003;118:4775–7.
- [47] Chen S, Lian J, Wang W, Jiang Y, Wang X, Chen S, Zeng P, Peng Z. Efficient deep blue electroluminescence with CIE (0.05–0.07) from phenanthroimidazole-acridine derivative hybrid fluorophores. J Mater Chem C 2018;6:9363–73.
 [48] Zeng W, Lai HY, Lee WK, Jiao M, Shiu YJ, Zhong C, Gong S, Zhou T, Xie G,
- [48] Zeng W, Lai HY, Lee WK, Jiao M, Shiu YJ, Zhong C, Gong S, Zhou T, Xie G, Sarma M, Wong KT, Wu CC, Yang C. Achieving nearly 30% external quantum

efficiency for orange–red organic light emitting diodes by employing thermally activated delayed fluorescence emitters composed of 1,8-naphthalimide-acridine hybrids. Adv Mater 2018;30:1704961.

- [49] Ye S, Wang Y, Guo R, Zhang Q, Lv X, Duan Y, Leng P, Sun S, Wang L. Asymmetric anthracene derivatives as multifunctional electronic materials for constructing simplified and efficient non-doped homogeneous deep blue fluorescent OLEDs. Chem Eng J 2020;393:124694.
- [50] Wang Y, Liu W, Ye S, Zhang Q, Duan Y, Guo R, Wang L. Molecular engineering of anthracene-based emitters for highly efficient nondoped deep-blue fluorescent OLEDs. J Mater Chem C 2020;8:9678–87.
- [51] Sheats JR, Antoniadis H, Hueschen M, Leonard W, Miller J, Moon R, Roitman D, Stocking A. Organic electroluminescent devices. Science 1996;273:884–8.
- [52] Xu Y, Wang C, Zhou X, Zhou J, Guo X, Liang X, Hu D, Li F, Ma D, Ma Y. Fine modulation of the higher-order excitonic states toward more efficient conversion from upper-level triplet to singlet. J Phys Chem Lett 2019;10:6878–84.