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Efficient Blue Organic Light-Emittng Diodes Based on Pyrene Phenanthrimidazole and

D-*π***-A** Chromophore

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Graphical abstract



Highlights

- Efficient organic light-emitting diodes (HyLEDs) have been fabricated with pyrene substituted phenanthroimidazole derivatives (Py-PPICN, Py-TPICN and Py-SPICN) as emissive layer.
- Among the pyrene phenanthrimidazoles, Py-SPICN based device shows excellent performances with maximum current efficiency of 3.41 cd A⁻¹, power efficiency of 2.80 lm W⁻¹ and EQE of 1.48 %.
- Also hybrid local and charge transfer (HLCT) state molecules ($D-\pi$ -A, TPA-PPICN and Cz-PPICN) have been designed by the incorporation of effective hot exciton RISC and high PL efficiency to maximize the external quantum efficiency of fluorescent OLEDs.
- The non doped device using Cz-TPICN dopant exhibits maximum current efficiency of 3.65 cd A⁻¹, power efficiency of 3.10 lmW⁻¹ and external quantum efficiency of 1.64 % with CIE coordinates of (0.15, 0.10).

Abstract

A series of phenanthroimidazole derivatives have been synthesized and used as non-doped blue emitters in organic light-emitting devices. Hybrid local and charge transfer (HLCT) state molecules (D- π -A) have been designed by the incorporation of effective hot exciton RISC and high PL efficiency to maximize the external quantum efficiency of fluorescent OLEDs. These compounds show high fluorescent quantum yield as well as good thermal and filmforming abilities. The emissive properties of the materials have been found to be related to the dihedral angles in these compounds. Among the pyrene substituted phenanthrimidazoles, Py-SPICN based device shows excellent performances with maximum current efficiency of

3.41 cd A^{-1} , power efficiency of 2.80 lm W $^{-1}$ and EQE of 1.48 %. The non doped device using Cz-TPICN dopant exhibits a maximum current efficiency of 3.65 cd A^{-1} , power efficiency of 3.10 lmW⁻¹ and external quantum efficiency of 1.64 % with Commission Internationale de'Eclairage (CIE) coordinates of (0.15, 0.10).

Key words: pyrene – phenanthrimidazoles; HLCT; hot exciton RISC; high quantum yield; excellent efficiencies.

1. Introduction

Development of highly efficient blue fluorescent materials instead of metal based triplet emitters is considered as an effective strategy for harvesting blue emission [1]. New generation of fluorescent materials without metal capable of converting non emissive triplet state excitons into emissive singlet excitons was developed to enhance the efficiency of fluorescent OLEDs [2]. Adachi et al. reported the thermally activated delayed fluorescence (TADF) materials with external quantum efficiency of 19.5% and CIE coordinates of (0.16, 0.20) [3]. However, internal electroluminescence quantum efficiency (η_{int}) of fluorescent materials is limited to 25% because of the singlet-triplet ratio. The three mechanisms namely, (i) thermally activated delayed fluorescence (TADF) [4], (ii) hybridized local and chargetransfer (HLCT) [5] as well as (iii) triplet-triplet annihilation (TTA) [6] are used to explain up-conversion technique of triplet excitons to singlet excitons in fluorescent OLEDs. Among them, TTA is considered as a promising triplet up-conversion technique providing a theoretical η_{int} of 62.5% only [7-10]. TADF is reported as an alternative of TTA to increase η_{int} after the efficient reverse intersystem crossing (RISC) with small energy gap between S₁ and T₁ (Δ Esr) [11-15].

Organic donor-spacer-acceptor compounds with hybridized local and charge transfer HLCT state exhibit high exciton utilization efficiency (η_S) in fluorescent OLEDs which can be attributed by hot exciton mechanism [16-18]. The external quantum efficiency (η_{EQE}) of devices can be calculated by: $\eta_{EQE} = \eta_{IQE} \times \eta_{out} = \eta_{rec} \times \eta_{PL} \times \eta_S \times \eta_{out}$, where η_{IQE} is internal quantum efficiency; η_{out} (~1/2n²) is light out coupling efficiency (n=1.5, $\eta_{out} \sim 20\%$); η_{rec} is efficiency for electron-hole recombination (100%); η_{PL} is photoluminescence efficiency of solid film and η_S is exciton utilization efficiency [$\eta_S = \eta_{rec} \times \eta_{PL} \times \eta_{out} \div$ η_{EL}] [19]. The low lying LE dominated HLCT state provides a high radiative rate for high photoluminescence efficiency (η_{PL}) of solid film whereas the high–lying CT dominated

HLCT state is responsible for high η_s through RISC process along with hot exciton mechanism [20]. The ambipolar nature of phenanthrimidazole derivatives have been shown as efficient deep blue emitters with fine color purities [21-24]. Devices with neutral pyrene group possesses neither strong electron donating ability nor electron accepting ability at C(2) of phenanthrimidazole are found rare, propensity to form excimers between pyrene in solid state and strong intramolecular charge transfer (ICT) [5, 18, 25-27].

In this work, we report a novel design strategy to construct deep-blue materials (Scheme 1), for highly efficient fluorescent devices. Among the Py-PPICN, Py-TPICN and Py-SPICN, the styryl pyrene core in Py-SPICN is expected to result excellent performances. Moreover, the twisted structure between the pyrene moiety and styryl group is beneficial to greatly reduce the excimer generation of pyrene and thus increase the quantum efficiency [28, 29]. The Cz and TPA units are introduced in the newly designed blue fluorescent materials with D- π -A architecture (TPA-TPICN and Cz-TPICN) to tune the emission toward the deep-blue region and with small ΔE_{ST} for blue phosphorescence. Herein, we report efficient deep blue emitters namely, pyren-4-(2-(4-phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-PPICN), pyren-4-(2-(5-thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-TPICN) and pyren-4-(2-(4-styryl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-SPICN) exhibit high photoluminescence quantum efficiency (Φ_{PL}). The HLCT materials with strong donor, triphenylamine (TPA) in 4-(2-(5-(4-(diphenylamino)phenyl)thiophen-2yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (TPA-TPICN) and weaker electron donating carbazole (Cz) in 4-(2-(5-(9H-carbazol-9-yl)thiophen-2-yl)-1H-phenanthro[9,10d]imidazol-1-yl)benzonitrile (Cz-TPICN) have also been reported. The Cz-TPICN is expected to decrease CT component with simultaneous increase of LE component in S1 HLCT state results low ΔE_{ST} and high ϕ_{PL} . The η_{PL} of Cz-TPICN film is enhanced compared to TPA-

TPICN film and thus combined effect of high η_{PL} and high η_S enhanced the η_{EQE} of Cz-TPICN based device.

2. Characterization:

Sigma-Aldrich supplied chemicals for synthesizing pyrene phenanthroimidazole derivatives, Py-PPICN, Py-TPICN and Py-SPICN and donor-spacer-acceptor derivatives, TPA-PPICN and Cz-PPICN (Scheme 1). NMR and mass spectroscopic measurements were obtained on Bruker spectrometer (400 MHz) and Agilent LCMS VL SD, respectively. The frontier energy levels are determined with oxidation potentials determined with CHI 630A potentiostat electrochemical analyzer (platinum electrode- working electrode; platinum wire-counter electrode; Ag/Ag⁺ electrode - reference electrode; scan rate -100 mV s⁻¹; 0.1M tetrabutylammoniumperchlorate in CH₂Cl₂ - supporting electrolyte). The Perkin Elmer (Lambda 35) instrument was used to measure absorption wavelength and diffused reflectance spectra (DRS) measurements were carried out using Lambda 35 spectrophotometer with RSA-PE-20 integrating sphere. Solvatochromic emission shifts were measured using LS55 fluorescence spectrometer (Perkin Elmer). The PL quantum yield (QY) was calculated with 0.5 M H₂SO₄ solution of quinine (0.54) as reference using the following equation: $\phi_{mk} = \phi_{vid}$

$$\left(\frac{I_{\text{unk}}}{I_{\text{std}}}\right) \left(\frac{A_{\text{std}}}{A_{\text{unk}}}\right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}}\right)^2 \left[\phi_{\text{unk}} - QY \text{ of unknown material; } \phi_{\text{std}} - QY \text{ of standard; } I_{\text{unk}} - \text{emission}$$

intensity of unknown material ; I_{std} - emission intensity of standard; A_{unk} - absorbance of unknown sample; A_{std} - absorbance of standard; η_{unk} - refractive index of the unknown material; η_{std} - refractive index of standard solution]. The QY of film was measured with integrating sphere (quartz plate). Decomposition temperature was measured with Perkin Elmer thermal analysis system (10° C min⁻¹; nitrogen flow rate - 100 mL min⁻¹). Glass transition temperature was recorded with NETZSCH (DSC-204) (10° C min⁻¹ under nitrogen atmosphere). The time correlated single photon counting (TCSPC) results fit to mono

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exponential decay, $f(t) = \alpha \exp(-t/\tau)$, where α and τ are respectively, the pre-exponential factor and lifetime of the various excited states involved. If N_i molecules are excited at zero time, the quantum yield of the i_{th} component α_i is proportional to the ratio $\alpha_i \tau_i / N_i$ and the α_i factors are related to the absorbance of the various substances at the excitation wavelength. Laser excitation was set at 270 nm and the fluorescence signal was measured at emission wavelength of individual compound. DAS6 software was used for the fit and the χ^2 values are less than 1.2.

3. Computational details:

All the density functional theory (DFT) calculations were carried out using Gaussian 09 package [30]. The density functional theory (DFT) and time-dependent DFT (TD-DFT) were carried out for the geometry optimization and the frequency calculation of ground state and excited state at the level of B3LYP/6-31G (d, p), respectively. In order to examine the nature of electronic transitions for excited states, natural transition orbitals (NTOs) are evaluated with the multifunctional wavefunction analyzer (Multiwfn) [31].

4. Fabrication of devices:

The devices based on the blue emitting phenanthrimidazoles were fabricated by vacuum deposition of the materials at 5 x 10^{-6} torr onto a clean glass precoated with a layer of indium tin oxide as the substrate with sheet resistance of 20 Ω /square. The glass was cleaned by sonication successively in a detergent solution, acetone, methanol and deionized water before use. Organic layers were deposited onto the substrate at a rate of 0.1 nm s⁻¹ and LiF was thermally evaporated onto the surface of organic layer. The thickness of the organic materials and the cathode layers were controlled using a quartz crystal thickness monitor. The device with the configuration of ITO/NPB (80 nm)/Py-PPICN (20 nm) or Py-TPICN (20 nm) or TPA-TPICN (20 nm) or Cz-TPICN (20 nm) or Py-SPICN (20 nm)/ Bphen (40 nm)/LiF (1 nm)/Al (120 nm) have been fabricated. NPB (4, 4'-bis [N-(1- naphthyl)-N-phenyl amino]

biphenyl) and BPhen (4,7-diphenyl- 1,10-phenanthroline) were used respectively, as hole transporting layer (HTL) and electron-transporting layer (ETL). Measurement of current, voltage and light intensity were made simultaneously using a Keithley 2400 sourcemeter. The EL spectra of the devices were carried out in ambient atmosphere without further encapsulations.

5. Experimental:

5.1. 4-(2-(4-bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BPPICN)

The product BPPICN was prepared by refluxing 9, 10-phenanthrenequinone (5 mmol), 4-bromobenzaldehyde (5 mmol), 4-aminobenzonitrile (6 mmol) and ammonium acetate (61 mmol) in acetic acid (20 mL) for 12 h under nitrogen atmosphere. The solvent was distilled off and the pure BPPICN was used. Yield 66%. M.P. 246 °C. Anal. calcd. for C₂₈H₁₆BrN₃: C, 70.90; H, 3.40; N, 8.86. Found: C, 70.82; H, 3.34; N, 8.79. ¹H NMR (400 MHz, CDCl₃): δ 7.28 (s, 2H), 7.32 (s, 1H), 7.41-7.44 (m, 4H), 7.72-7.75 (m, 4H), 7.89 (d, J=8.5 Hz, 2H), 8.59 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 112.74, 118.04, 119.32, 123.51, 123.53, 123.56, 123.53, 123.59, 123.63, 126.62, 126.65, 128.43, 132.47, 138.64, 146.34. MALDI–TOF MS: m/z.474.36 [M+]. calcd.474.40.

5.2. 4-(2-(5-bromothiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BTPICN)

The compound BTPICN was prepared using the methodology similar to that of BPPICN by replacing 4-bromobenzaldehyde with 5-bromothiophene-2-carbaldehyde. Yield 67%. M.P. 226 °C. Anal. calcd. for C₂₆H₁₄BrN₃S: C, 65.01; H, 2.95; N, 8.75;. Found: C, 65.21; H, 3.02; N, 8.68. ¹H NMR (400 MHz, CDCl₃): δ 6.62 (s, 2H), 6.83 (s, 1H), 7.34-7.39 (m, 4H), 7.69-7.72 (m, 4H), 7.92 (s, 2H), 8.48 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 109.13, 113.17, 119.72, 123.92, 123.94, 123.97, 124.03, 124.12, 124.96, 125.62, 126.43, 128.84, 128.86, 130.41, 130.44, 138.83, 139.03, 144.03. MALDI–TOF MS: m/z. 480.40 [M+]. calcd.480.45.

5.3. 4-(2-(4-bromostyryl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BSPICN)

The compound BSPICN was prepared using the methodology similar to that of BPPICN by replacing 4-bromobenzaldehyde with 4-bromocinnamaldehyde. Yield 64%. M.P. 258 °C. Anal. calcd. for C₃₀H₁₈BrN₃: C, 72.06; H, 3.67; N, 8.47. Found: C, 72.73; H, 3.95; N 8.56. ¹H NMR (400 MHz, CDCl₃): δ 6.89 (d, J=8.6 Hz, 2H), 6.97 (d, J=16.2 Hz, 1H), 7.06-7.23 (m, 4H), 7.31 (d, J=14.6 Hz, 2H) 7.65-7.73 (m, 5H), 8.08 (d, J=9.4 Hz, 1H), 8.21 (d, J=8.8 Hz, 2H), 8.5 (d, J=8.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): 117.84, 122.59, 123.02, 123.47, 123.94, 124.28, 124.62, 126.01, 126.28, 127.09, 127.26, 128.33, 128.42, 128.57, 129.15, 129.43, 129.49, 129.72, 130.88, 132.89, 134.41, 149.83. MALDI–TOF MS: m/z 500.42 [M+]. calcd.500.38.

5.4. Pyren-4-(2-(4-phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-PPICN)

A mixture of 4-(2-(4-bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BPPICN) (4.5 mmol), pyren-4-yl-4-boronic acid (7.5 mmol), Pd(PPh₃)₄ (0.25 mmol) and aqueous Na₂CO₃ (15 mL) in toluene:ethanol (20:15 mL) was refluxed in nitrogen atmosphere for 18 h. The solvent was distilled off and the pure Py-PPICN was used further analysis. Yield 62%. M.P. 289 °C. Anal. calcd. for C₄₄H₂₅N₃: C, 70.90; H, 3.40; N, 8.86. Found: C, 88.72; H, 4.23; N, 7.05. ¹H NMR (400 MHz, CDCl₃): δ 7.38 (s, 2H), 7.49 (s, 2H), 7.52-7.56 (m, 4H), 7.69 (s, 4H), 7.77-7.83 (m, 7H), 7.98 (s, 1H), 8.08-8.11(m,4H), 8.74(s,2H). ¹³C NMR (100 MHz, CDCl₃): 113.17, 116.82, 121.99, 124.12, 125.96, 126.22, 126.45, 126.78, 127.32, 127.52, 127.57, 127.61, 127,63, 127.67, 128.51, 129.11, 129.39, 129.43, 129.82, 130.68, 132.15, 132.58, 133.37, 134.49, 135.12, 137.61, 142.78, 150.32. MALDI–TOF MS: m/z 595.66 [M+]. calcd. 595.70.

5.5. Pyren-4-(2-(5-thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-TPICN)

The compound Py-TPICN was prepared using the methodology similar to that of Py-PPICN by replacing BPPICN with BTPICN. Yield 58%. M.P. 256 °C. Anal. calcd. for C₄₂H₂₃N₃S: 601.7; C, 83.83; H, 3.85; N, 6.98. Found: C, 70.82; H, 3.34; N, 8.79. ¹H NMR (400 MHz, CDCl₃): δ 6.97(s, 2H), 7.38-7.41 (m, 4H), 7.68 (s, 3H), 7.76-7.81 (m, 6H), 7.92 (s, 1H), 8.01-8.07 (m, 4H), 8.82 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 110.15, 114.19, 120.74, 124.97, 124.99, 125.02, 125.05, 125.14, 125.98, 126.64, 127.45, 127.51, 127.54, 127.59, 127.63, 129.86, 129.88, 131.42, 131.46, 139.85, 140.05, 14.05. MALDI–TOF MS: m/z 601.78 [M+]. calcd. 601.70.

The compound Py-SPICN was prepared using the methodology similar to that of Py-PPICN by replacing BPPICN with BSPICN. Yield 61%. M.P. 296 °C. Anal. calcd. for C₄₆H₂₇N₃: C, 88.86; H, 4.38; N, 6.76. Found: C, 88.72; H, 4.33; N, 6.65. ¹H NMR (400 MHz, CDCl₃): δ 6.78 (d, J=16.6 Hz, 2H), 7.23 (d, J=15.4 Hz, 2H), 7.38-7.43 (m, 6H), 7.64 (s, 4H), 7.76-7.89 (m, 5H), 7.86 (s, 2H), 8.06 (d, J=8.2 Hz, 2H), 8.14 (s, 1H), 8.72(s, 2H). ¹³C NMR (100 MHz, CDCl₃): 110.61, 111.29, 114.33, 119.38, 120.92, 123.53, 124.79, 124.83, 125.04, 125.06, 125.10, 125.13, 125.16, 125.41, 126.09, 126.14, 126.30, 126.34, 126.81, 130.04, 130.78,

Pyren-4-(2-(4-styryl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (Py-SPICN)

5.6.

130.81, 131.59, 131.67, 134.21, 140.01, 124.21. MALDI–TOF MS: m/z 621.66 [M+]. calcd. 621.7.

5.7. 4-(2-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (TPA-TPICN)

A mixture of 4-(2-(5-bromothiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BTPICN) (4.5 mmol), 4-(diphenylamino)phenylboronic acid (7.5 mmol), Pd(PPh₃)₄ (0.25 mmol) and aqueous Na₂CO₃ (15 mL) in toluene:ethanol (20:15 mL) was refluxed in nitrogen

atmosphere for 18 h. The reaction mixture was extracted with dichloromethane. The solvent was distilled off and the pure TPA-TPICN was used further analysis. Yield 61%. M.P. 298 °C. Anal. calcd. for C₃₈H₂₂N₄S: C, 80.54; H, 3.91; N, 9.89. Found: C, 80.42; H, 3.88; N, 9.76. ¹H NMR (400 MHz, CDCl₃): δ 6.38-6.42 (m, 4H), 6.52 (s, 2H), 6.58 (s, 2H) 76.92-6.97 (m, 6H), 7.18 (s, 1H), 7.48 (s, 2H), 7.51 (s, 2H), 7.78-7.83 (m, 4H), 8.07 (s, 2H), 8.57 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 113.62, 116.53, 119.17, 121.26, 122.03, 122.10, 122.17, 124.71, 124.80, 124.97, 125.01, 125.76, 126.45, 127.27, 127.35, 127.40, 127.47, 127.52, 128.64, 129.78, 129.83, 131.27, 131.36, 138.65, 138.71, 139.88, 139.94, 141.28. MALDI–TOF MS: m/z 644.78 [M+], calcd. 644.72.

5.8. 4-(2-(5-(9H-carbazol-9-yl)thiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1yl)benzonitrile (Cz-TPICN)

A mixture of 4-(2-(5-bromothiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BTPICN) (4.5 mmol), 9H-carbazole (7.5 mmol), CuI (10.0 mg, 0.05 mmol), 18-crown-6 (13.2 mg, 0.05 mmol), and K₂CO₃ (0.83 g, 6.0 mmol) in tetrahydro-1,3-dimethylpyrimidin-2(1H)-one (2.0 mL) was refluxed in nitrogen atmosphere for 18 h. The solvent was distilled off and the pure Cz-TPICN was used further analysis. Yield 57%. M.P. 300 °C. Anal. calcd. for C₃₈H₂₂N₄S: C, 80.54; H, 3.91; N, 9.89. Found: C, 80.42; H, 3.88; N, 9.76. ¹H NMR (400 MHz, CDCl₃): δ 6.89 (s, 2H), 6.92 (s, 1H), 7.38-7.42 (m, 6H), 7.48-7.56 (m, 4H), 7.76 (s, 1H), 7.89-7.94 (m, 4H), 8.02 (s, 2H), 8.62 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): 108.27, 108.34, 114.72, 117.58, 117.67, 118.81, 118.88, 119.12, 121.37, 122.14, 122.21, 122.28, 124.82, 124.91, 125.08, 125.12, 125.87, 126.58, 127.38, 127.46, 127.51, 127.58, 127.63, 128.76, 129.81, 131.37, 131.41, 138.78, 139.97. MALDI–TOF MS: m/z 566.67 [M+]. calcd. 566.58.

6. Results and Discussion

6.1. Photophysical properties of pyrene phenanthroimidazole derivatives

The synthetic route of pyrene phenanthroimidazole derivatives, Py-PPICN, Py-TPICN and Py-SPICN and donor-spacer-acceptor derivatives, TPA-TPICN and Cz-TPICN with their chemical structures are shown in Scheme 1. The pyrene phenanthroimidazole derivatives (Py-PPICN, Py-TPICN and Py-SPICN) were prepared via Suzuki coupling reaction between BPPICN or BTPICN or BSPICN and pyrenyl-1-boronic acid with a yield of 62, 58 and 60 % of Py-PPICN, Py-TPICN and Py-SPICN, respectively. BTPICN on reaction with diphenylaminophenylboronic acid or 9H-carbazole with appropriate condition yield TPA-TPICN and Cz-TPICN, respectively. All these synthesized materials were characterized by ¹H and ¹³C NMR, high resolution mass and elemental analysis. The thermal properties of blue light emitting materials have been analysed using TGA and DSC under a nitrogen atmosphere to understand the device stability. The pyrene phenanthroimidazole derivatives (Py-PPICN, Py-TPICN and Py-SPICN) exhibit excellent thermal properties: decomposition temperature (T_d) of 420, 404 and 422 °C, high melting temperature (T_m) of 289, 256 and 296, °C and glass transition temperature (Tg) of 110, 130 and 150 °C due to the non-coplanar geometry exhibited by bulky and rigid pyrene group. For Cz-TPICN, the glass transition temperature (T_g) and thermal decomposition temperature (T_d) were measured as 154 and 436 °C which are higher than that of TPA-TPICN ($T_g - 150$ and $T_d - 428$ °C) (Figure 1). The higher thermal stability of Cz-TPICN is due to the stronger rigidity of Cz than TPA which will be in favour of OLED stability. From the cyclic voltammogram of Cz-TPICN and TPA-TPICN, the HOMO and LUMO energies have been calculated (Figure 2). The LUMO energies of both Cz-TPICN (-2.72 eV) and TPA- TPICN (-2.67 eV) are nearly same which is attributed to their same acceptor TPICN unit. The HOMO energy (-5.38 eV) of Cz-TPICN is lower than that of TPA-TPICN (-5.23 eV) corresponding to that of Cz and TPA group,

respectively. The decreased HOMO energy of Cz-TPICN is due to the poor electron donating ability of Cz relative to TPA and this observation was supported by DFT calculation. On comparison with Py-TPICN and Py-SPICN, the weaker electron donating ability of the phenyl ring in Py-PPICN rendering with a shallow HOMO energy level results higher energy gap. Key thermal and photophysical data of the two compounds are summarized in Table 1.

The ground state (S₀) and excited state (S₁) geometries were optimized using DFT/B3LYP/6–31G (d, p) and TD–DFT/B3LYP/6–31G (d, p) methods for Py-PPICN, Py-TPICN, Py-SPICN TPA-TPICN and Cz-TPICN are displayed in Figure 3. The optimized geometry of Py-PPICN, Py-TPICN and Py-SPICN shows that the phenyl in Py-PPICN, thiophene in Py-TPICN and styryl in Py-SPICN rings and the phenanthroimidazole ring adopt an almost coplanar configuration with a dihedral angle (θ_2) of 7.7, 3.8 and 2.2° leading to an extended molecule. The bulky and rigid pyrene ring is twisted about the phenyl (Py-PPICN), thiophene (Py-TPICN) and styryl (Py-SPICN) rings with dihedral angle (θ_3) of 98.83, 106.2 and 110.6° (Table 2). The benzonitrile ring is twisted about the phenanthroimidazole ring with a dihedral angle (θ_1) of 62.5 (Py-PPICN), 73.4 (Py-TPICN) and 88.6° (Py-SPICN). The electron donating aryl rings and the electron accepting phenanthrimidazole moieties would lead to intermolecular electrostatic interaction [32]. The dihedral angle (θ_3) between the aryl rings and bulky pyrene moieties is an important parameter, since large dihedral angle can suppress intermolecular π – π stacking in solid state and thus prevent self-quenching of fluorescence.

In the ground state geometry of donor-spacer-acceptor materials (TPA-TPICN and Cz-TPICN), the benzonitrile fragment (θ_1) and thiaphene (θ_2) are highly twisted about phenanthrimidazole plane with dihedral angle of θ_1 -72.6°; θ_2 -26.6° for TPA-TPICN and θ_1 -76.5°; θ_2 -30.2° for Cz-TPICN. The TPA moiety in TPA-TPICN and Cz moiety in Cz-TPICN also twisted with dihedral angle of 40.5° and 39.8°, respectively [33]. The larger twist angle

of Cz-TPICN when compared with TPA-TPICN is due to the stronger repulsion between the two adjacent hydrogen atoms in carbazole and phenyl ring, as a result of the stronger rigidity of Cz than TPA. The excited state twist angle θ_2 of Cz-TPICN and TPA-TPICN are increased to 40.4° and 30.4°, respectively, when compared with ground state twist angle θ_1 . Similarly smaller twist angle θ_1 was obtained for Cz-TPICN when compared with TPA-TPICN. The bond length (R₁) of Cz-TPICN and TPA-TPICN are elongated by 0.04 and 0.09 Å, respectively from S₀ to S₁. The smaller change of geometry from S₀ to S₁ in Cz moiety of Cz-TPICN than that of TPA unit in TPA-TPICN may decrease the non radiative emission (*k_{nr}*) results enhancement of photoluminance efficiency.

6.2. Photophysical properties:

The absorption spectra of Py-PPICN, Py-TPICN and Py-SPICN in solution and the solid film spectra of pyrene substituted phenanthrimidazole suggest that intermolecular interaction in solid is weak (Figure 4). The D- π -A derivatives TPA-TPICN and Cz-TPICN exhibits higher blue shift with higher molar absorptivity when compared to pyrene phenanthrimidazoles Py-PPICN, Py-TPICN and Py-SPICN and this might be due to the presence of strong and weak electron donar triphenylamine and carbazole moieties [34] expected to increase the efficiencies. Blue emission at 420, 440 and 450 nm and absorption at 260, 264 and 269 nm in solid film state was observed and the blue-shift of the PL spectra of Py-PPICN compared with Py-TPICN and Py-SPICN might be due to the weaker electron donating property of the phenyl ring rendering with a deeper HOMO energy and thus a higher energy gap in Py-PPICN. Key thermal and photophysical data of the two compounds are summarized in Table 1. It is well known that efficient carrier injection at interfaces between different layers in OLED is essential for obtaining high performance devices. It is thus important for the emissive layer to possess a shallow HOMO for facilitating hole-injection. The electronic energies (HOMO and LUMO) of the non-doped blue emitters such

as Py-PPICN, Py-TPICN and Py-SPICN have been examined by cyclic voltammetry (CV) and the redox potentials have been measured from the plot potential versus current which is shown in Figure 5a. CV analysis exhibits one quasi-reversible oxidation wave with an oxidative onset potential of 0.40 V (Py-PPICN), 0.36 V (Py-TPICN) and 0.30 V (Py-SPICN) which gives the HOMO energies of -5.20 eV (Py-PPICN), -5.16 eV (Py-TPICN) and -5.10 eV (Py-SPICN) by comparison to ferrocene ($E_{HOMO} = E_{ox} + 4.8 \text{ eV}$) [35]. The LUMO energies have been deduced from HOMO energies and the lowest-energy absorption edges of the UV-vis absorption spectra [36]. The LUMO energies, -2.44 eV (Py-PPICN), -2.60 eV (Py-TPICN) and -2.54eV (Py-SPICN) are almost close to that of 1, 3, 5-tris (Nphenylimidazol-2-yl) benzene (TPBI) revealing that the electron injection abilities of Py-PPICN, Py-TPICN and Py-SPICN are similar to TPBI. This reflects the more balanced carrier injection properties of these materials. The electron density distribution of the HOMO is localized predominantly on the electron rich pyrene with aryl rings and the HOMO values are ranging from -5.20 to -5.10 eV. The electron density of LUMO is distributing on the phenanthrimidazole plane (Figure 2) but their values are changed from -2.44 to -2.60 eV. As our expectation, some degree of space charge separation ability is found which would be benefit for the injection of carriers from electrode. To analyse the relative contribution of radiative and non-radiative relaxation processes in the excited state deactivation the radiative (τ_r) and nonradiative (τ_{nr}) decay time constants were calculated (Figure 5b and 5c). The calculated constants [$\tau_r = \tau/\Phi$: 9.33 ns (Py-PPICN); 9.60 ns (Py-TPICN) and 9.81 ns (Py-SPICN); $\tau_{nr} = \tau/(1-\Phi)$:7.63 ns (Py-PPICN); 10.0 ns (Py-TPICN) and 12.0 ns (Py-SPICN). These values reveal that increased polarity of the substituents was found to strongly affect τ_r of the phenanthrimidazole derivatives while influencing τ_{nr} at a much lesser degree.

The excited state properties of TPA-TPICN and Cz-TPICN materials have been investigated from their photophysical properties (Figure 4). The absorption peak at 248 and

252 nm for TPA-TPICN and Cz-TPICN, respectively and their emission maxima was observed at 410 and 401 nm in dichloromethane solution (Table 1). Compared with TPA-TPICN, Cz-TPICN exhibit blue shift for both UV-vis (4 nm) and PL (9 nm) spectra which can be attributed to poor electron donor ability of Cz relative to TPA. Increased LE component with simultaneous decrease of CT component in S₁ emissive state is likely to be the reason for this blue shift. The full width at half maximum in absorption spectrum of Cz-TPICN (32 nm) is narrowed relative to that of TPA-TPICN (42 nm). This observation also supports the decrease CT component of Cz-TPICN in S₁ state which is in good agreement with NTO description for S₀ \rightarrow S₁ transition [37]. This blue shift can be attributed to the enhanced LE component which is equivalent to the suppressed CT component in the emissive states of TPA-TPICN and Cz-TPICN. The extension of LE component expected to results red shift of PL spectrum whereas suppressed CT component results blue shift of PL spectrum. From the experimental observation it is known that the latter factor is more dominant than the former one.

6.3. Solvatochromic Effects

The intramolecular charge transfers of both TPA-TPICN and Cz-TPICN in excited states have been analyzed by solvatochromic effect [17, 18]. The emission spectra of Cz-TPICN exhibits solvatochromic effect with increase of solvent polarity and the total red shift of 43 nm is smaller than that of TPA-TPICN (74 nm) (Figure S1). Similarly a small shift of 12 nm and 20 nm has been observed for Cz-TPICN and TPA-TPICN, respectively in the absorption spectra. The solvatochromic shifts reveal that the low lying excited state (S1) of the Cz-TPICN and TPA-TPICN must possesses CT character [38-40]. The percentage of CT character of Cz-TPICN is lower than that in TPA-TPICN and the percentage of LE character for Cz-TPICN is higher than that in TPA-TPICN. The solvatochromic shift of Cz-TPICN (43 nm) is smaller than that of TPA-TPICN (74 nm) from hexane to acetonitrile. In hexane, both

TPA-TPICN and Cz-TPICN show LE like character because of the existence of the vibronic PL spectrum. The quantum yield of Cz-TPICN (ϕ sol/film : 0.70/0.65) is higher than that of TPA-TPICN (ϕ sol/film : 0.62/0.60) as a result of enhanced LE component in emissive state. The large blue shift relative to TPA-TPICN indicates that Cz-TPICN is a potential pure blue OLED emitter (Table 1).

The excited state dipole moment (μ_e) of TPA-TPICN and Cz-TPICN have been calculated from the Lippert-Mataga plot of Stokes shift (v_a-v_f) against orientation polarizability, $f(\varepsilon, n)$ (Figure 5d) (Tables S1 and S2) [41]. Both compounds show two independent slopes of two section fitted lines which reveal the existence of two different characters of excited state [42]. The dipole moment was calculated to be 19.9 (R^2 - 0.95) and 9.1 D (R² - 0.96) (Cz-TPICN) and 21.4 (R² - 0.94) and 13.0 D (R² - 0.97) (TPA-TPICN) for high and low polar solvents, respectively. In low polar solvents, the dipole moment of 9.1 D (Cz-TPICN) and 13.0 D (TPA-TPICN) reveal that the S1 state possessed CT character in addition to LE. The quantum yield of both TPA-TPICN and Cz-TPICN decreases with increasing solvent polarity and high quantum yield was obtained between hexane and butyl ether. These factors demonstrated that certain degree of locally excited (LE) character has been introduced thus, S₁ state in low polar solvents contained both CT and LE components. However, observation of single-exponential fluorescence decay (Figure 5c) for TPA-TPICN and Cz-TPICN in low polar solvents reveal that a new and unique excited state *i.e.*, hybridized local and charge-transfer (HLCT) state exists in the D- π -A architecture rather than a mixture of LE and CT states [43, 44]. In low polarity solvent, the smaller μ_e of Cz-TPICN relative to TPA-TPICN can be ascribed to weak donor ability of Cz than TPA corresponding to the higher LE proportion as expected in molecule design of Cz-TPICN.

The two section linear relation between Stokes shift and solvent polarity indicating that both Cz-TPICN and TPA-TPICN possess an intercrossed excited state of LE and CT: a

higher contribution from CT state in high polarity solvents, whereas a dominant contribution from LE state in low polarity solvents. The intercrossed excited state of the LE and CT may occur in a moderate polarity between butyl ether and ethyl acetate. The hybridized local and charge transfer (HLCT) state forms due to the intercrossing coupling between LE and CT states. The lifetime measurement reveals that this intercrossed excited state in different polar solvents should be a hybridized local and charge transfer state (HLCT) instead of two species state through a simple addition of LE and CT (Figure 6). The emission wavelength of both TPA-TPICN and Cz-TPICN in film is close to that in ethyl ether which supports the HLCT state formed in TPA-TPICN and Cz-TPICN film. The radiative transition rate (k_{r}) and the non–radiative transition rate (k_{nr}) of TPA-TPICN and Cz-TPICN have been calculated from lifetime and quantum yield. Compared with TPA-TPICN, the k_r of Cz-TPICN is increased and k_{nr} is decreased. This result is also in good agreement with the aim of our molecular design.

The oscillator strength of S₁ state of Cz-TPICN (0.8861, Table S3) is higher than that of TPA-TPICN (0.5123, Table S3) results higher photoluminance efficiency (η_{PL}). Chemical modification from TPA to Cz induces an increase of LE component in S₁ emissive state together with rigid molecular skeleton. Both S₁ and S₂ states exhibit a character of hybridized local and charge transfer state (HLCT) in which higher LE character of S₁ state enhance the η_{PL} in Cz-TPICN. Density functional theory calculations combined with the natural transition orbital analysis were used to describe the excited state properties of TPA-TPICN and Cz-TPICN materials (Figure 7). For both the materials, the S₁ state holes are delocalized over the horizontal backbone while particles are mainly localized on the vertical benzonitrile. As a comparison, a similar CT transition character is maintained from the horizontal backbone to the vertical benzonitrile in the S₁ state of both TPA-TPICN and Cz-TPICN. The overlap density between hole and particle is significantly expanded due to the insertion of spacer

styryl moiety indicating an enhanced LE component in S₁ state (Figure 7). The NTO of S₁ and S₂ excited states of both TPA-TPICN and Cz-TPICN exhibit a hybrid splitting state character that derives from the interstate coupling between LE and CT states (Figure 7). NTO analysis shows that both S₁ and S₂ states demonstrate HLCT characters. The wave function symmetry of the particle on the benzonitrile group are just in opposite phase between S1 and S2 states indicating that the interstate hybirdization coupling occurs through the positive and negative linear combination of horizontal LE and vertical CT respectively, $\Psi_{S1/S2} = c_{LE} \cdot \Psi_{LE} \pm c_{CT} \cdot$ Ψ_{CT} . The more similar hole-electron wave function between S1 and S2 is observed in both TPA-TPICN and Cz-TPICN which indicates a quasi-equivalent hybridization between LE and CT states, as a result of their almost isoenergies of initial LE and CT states (Figure 8). Therefore, the degree of hybridization between LE and CT states is dependent not only the initial ELE-ECT energy gap but also their interstate coupling strength [45]. Compared with the non-equivalent hybridization, the quasi-equivalent hybridization is expected to achieve the combination of high η_{PL} and high η_s to maximize the EL efficiency of the fluorescent OLED materials due to the more balanced LE and CT components in HLCT state of TPA-TPICN and Cz-TPICN.

The triplet excitons can be converted into the singlet excitons in TPA-TPICN and Cz-TPICN through a RISC process with a high lying excited state (hot CT channel) [46, 47]. The hot CT channel is beneficial to the triplet exciton conversion in EL process without any delayed fluorescence. In EL process, the intermolecular CT excitons are generated with weak binding energy on the higher excited states and the triplet exciton can be converted into the singlet one along the hot CT channel [48]. As a result, the exciton utilization can be harvested in TPA-TPICN and Cz-TPICN like phosphorescent materials. The quasi-equivalently hybridized material TPA-TPICN and Cz-TPICN exhibits excellent device performances, as a result of fine modulation in excited states: due to the enhanced LE component and sufficient

hybridization between LE and CT components high η_{PL} and high η_s are achieved. The coexisting LE and CT characters in TPA-TPICN and Cz-TPICN harvested high η_{PL} and high η_s and enhanced the OLEDs performances.

6.4. Electroluminescent studies

Energy-level diagram of the materials used for the fabrication of device are shown in Figure 9. The TADF material exhibit flat decay curve due to the time consuming TADF process for the exciton conversion from triplet to singlet. In the present case TPA-TPICN and Cz-TPICN shows sharp decay curve reveal that the radiative excitons in TPA-TPICN and Cz-TPICN are short-lived component without TADF contribution (Figure S2). The exciton utilization efficiency (η s) in TPA-TPICN and Cz-TPICN are of neither TTA nor TADF mechanisms [49].

The non-doped EL device have been fabricated to investigate the relationship between excited state properties and the EL performances of TPA-TPICN and Cz-TPICN are displayed in Figure 10 (Table 3). The device with the configuration of ITO/NPB (80 nm)/Py-PPICN (20 nm) or Py-TPICN (20 nm) or TPA-TPICN (20 nm) or Cz-TPICN (20 nm) or Py-SPICN (20 nm)/ Bphen (40 nm)/LiF (1 nm)/Al (120 nm) have been fabricated. The electroluminescence (EL) spectra of the three devices based on pyrene substituted phenanthrimidazoles Py-PPICN, Py-TPICN and Py-SPICN and TPA-TPICN and Cz-TPICN are similar to their PL spectra which shows both EL and PL originate from the same radiative decay of the singlet excitons (Figure S2). Among the pyrene substituted phenanthrimidazoles, Py-SPICN based device shows excellent performances with maximum current efficiency of $3.41 \text{ cd } A^{-1}$, maximum power efficiency of 2.80 lm W^{-1} and maximum EQE of 1.48 %. The fabricated devices exhibit blue EL emission with the CIE coordinates of TPA-TPICN (0.16, 0.12) and Cz-TPICN (0.15, 0.10). The Cz-TPICN based device shows excellent performances with maximum current efficiency of $3.65 \text{ cd } A^{-1}$, maximum power efficiency of 3.10 lm W^{-1}

and maximum EQE of 1.64 %. The maximum η_s 13.0 % (TPA-TPICN) and 12.6 % (Cz-TPICN) of EL devices can be estimated using the equation $\eta_s = \eta_{res} \times \eta_{PL} \times \eta_{out} \div \eta_{EL}$, where η out ($\approx 1/2n^2$) is the light out coupling efficiency ($\approx 20\%$); η_{rec} is the efficiency for electron hole recombination (100 %) [20]. The increased η_s and η_{IQE} 7.8 % (TPA-TPICN); 8.2 % (Cz-TPICN) harvested in TPA-TPICN and Cz-TPICN is due to the maintained CT component from the cyano substitution. The device efficiencies are compared with already reported [50-60] non-doped emitters efficiencies (Table S4), which shows that the newly synthesized blueemissive materials, Py-PPICN, Py-TPICN and Py-SPICN and D- π -A architecture, TPA-TPICN and Cz-TPICN are among the best in terms of efficiencies.

7. Conclusion

Blue-emissive materials, Py-PPICN, Py-TPICN and Py-SPICN have been developed based on pyrene and phenanthro[9,10-d]imidazole functional core. These materials exhibit high fluorescence quantum yield as well as good thermal and film-forming abilities. Py-SPICN based device shows excellent performances with maximum current efficiency of 3.41 cd A^{-1} , power efficiency of 2.80 lm W^{-1} and EQE of 1.48 %. The photophysical and electrochemical properties of blue fluorescent materials with D- π -A architecture, TPA-TPICN and Cz-TPICN can be tuned by chemical modification of strong donor TPA moiety by weak donor Cz moiety, which results HLCT as the emissive state with increased LE and decreased CT which in turn increased the quantum efficiency of 3.65 cd A^{-1} , maximum power efficiency of 3.10 lm W^{-1} and maximum EQE of 1.64 %. The devices exhibit blue EL emission with the CIE coordinates of TPA-TPICN (0.16, 0.12) and Cz-TPICN (0.15, 0.10).The HLCT state molecules with hot exciton RISC provide a new strategy to design the next-generation organic electroluminescent materials with low-cost and high device performances.

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Reference:

- [1] L. Xiao, S. J. Su, Y. Agata, H. Lan, J. Kido, Nearly 100% Internal Quantum Efficiency in an Organic Blue-Light Electrophosphorescent Device Using a Weak Electron Transporting Material with a Wide Energy Gap, Adv.Mater. 21 (2009) 1271.
- [2] Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, Thermally Activated Delayed Fluorescence Materials towards the Breakthrough of Organoelectronics, Adv. Mater. 26 (2014) 7931.
- [3] Q. Zhang, B. Li, Huang S, H. Nomura, H. Tanaka, C. Adachi, Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence Nat. Photonics. 8 (2014) 326.
- [4] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Highly efficient organic lightemitting diodes from delayed fluorescence Nature. 492 (2012) 234.
- [5] S. Zhang, L. Yao, Q. Peng, W. J. Li, Y. Pan, R. Xiao, Y. Gao, C. Gu, Z. Wang, P. Lu, F. Li, S. Su, B. Yang, Y. Ma, Achieving a Significantly Increased Efficiency in Nondoped Pure Blue Fluorescent OLED: A Quasi-Equivalent Hybridized Excited State, Adv. Funct. Mater. 25 (2015) 1755.
- [6] Y. Tamai, H. Ohkita, H. Benten, S. Ito, Triplet Exciton Dynamics in Fluorene–Amine Copolymer Films, Chem. Mater. 26 (2014) 2733.

- [7] K. Okumoto, H. Kanno, Y. Hamada, H. Takahashi, K. Shibata, Green fluorescent organic light-emitting device with external quantum efficiency of nearly 10%, Appl. Phys. Lett. 89 (2006) 063504.
- [8] D. Y. Kondakov, Characterization of triplet-triplet annihilation in organic light-emitting diodes based on anthracene derivatives, J. Appl. Phys. 102 (2007) 114504.
- [9] D. Y. Kondakov, T. D. Pawlik, T. K. Hatwar, J. P. Spindler, Triplet annihilation exceeding spin statistical limit in highly efficient fluorescent organic light-emitting diodes, J. Appl. Phys. 106 (2009) 124510.
- [10] H. Fukagawa, et al., Anthracene derivatives as efficient emitting hosts for blue organic light-emitting diodes utilizing triplet-triplet annihilation, Org. Electron. 13 (2012) 1197.
- [11] A. Endo, et al., Thermally Activated Delayed Fluorescence from Sn⁴⁺–Porphyrin Complexes and Their Application to Organic Light Emitting Diodes — A Novel Mechanism for Electroluminescence, Adv. Mater. 21 (2009) 4802.
- [12] A. Endo, et al., Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes, Appl. Phys. Lett. 98 (2011) 083302.
- [13] T. Nakagawa, S. Y. Ku, K. T. Wong, C. Adachi, Electroluminescence based on thermally activated delayed fluorescence generated by a spirobifluorene donor–acceptor structure, Chem. Commun. 48 (2012) 9580.
- [14] S. Y. Lee, T. Yasuda, H. Nomura, C. Adachi, High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor– acceptor hybrid molecules, Appl. Phys. Lett. 101 (2012) 093306.
- [15] Q. Peng, et al., Evidence of the Reverse Intersystem Crossing in Intra-Molecular Charge-Transfer Fluorescence-Based Organic Light-Emitting Devices through Magneto-Electroluminescence Measurements, Adv. Opt. Mater. 1 (2013) 362.

- [16] W. J. Li, D.D. Liu, F.Z. Shen, D.G. Ma, Z.M. Wang, T. Fei, B. Yang, Y.G. Ma, A Twisting Donor-Acceptor Molecule with an Intercrossed Excited State for Highly Efficient, Deep-Blue Electroluminescence, Adv. Funct. Mater. 22 (2012) 2797.
- [17] W. J. Li, Y. Y. Pan, R. Xiao, Q. M. Peng, S. T. Zhang, D. G. Ma, F. Li, F. Z. Shen, Y. H. Wang, B. Yang, Y. G. Ma, Employing ~100% Excitons in OLEDs by Utilizing a Fluorescent Molecule with Hybridized Local and Charge-Transfer Excited State, Adv. Funct. Mater. 24 (2014) 1609.
- [18] S. Tang, W. J. Li, F. Z. Shen, D. D. Liu, B. Yang, Y. G. Ma, Highly efficient deep-blue electroluminescence based on the triphenylamine-cored and peripheral blue emitters with segregative HOMO–LUMO characteristics, J. Mater. Chem. 22 (2012) 4401.
- [19] J. R. Sheats, H. Antoniadis, M. Hueschen W. Leonard, J. Miller, R. Moon, D. Roitman,A. Stocking, Organic electroluminescent devices, Science. 273 (1996) 884.
- [20] D. Chaudhuri, E. Sigmund, A. Meyer, L. Rcck, P. Klemm, S. Lautenschlager, A. Schmid, S. R. Yost, T. Van, S. Bange, S. Hcger, J. M. Lupton, Metal-Free OLED Triplet Emitters by Side-Stepping Kasha's Rule, Angew. Chem. 52 (2013) 13449.
- [21] X. Ouyang, X. Li, L. Ai, D. Mi, Z. Ge, S. J. Su, Novel "Hot Exciton" Blue Fluorophores for High Performance Fluorescent/Phosphorescent Hybrid White Organic Light-Emitting Diodes with Superhigh Phosphorescent Dopant Concentration and Improved Efficiency Roll-Of, Appl. Mater. Interfaces. 7 (2015) 7869.
- [22] K. Wang, S. Wang, J. Wei, Y. Miao, Y. Liu, Y. Wang, Novel diarylborane– phenanthroimidazole hybrid bipolar host materials for high-performance red, yellow and green electrophosphorescent devices, Org. Electron. 15 (2014) 3211.
- [23] N. Su, F. Meng, J. Chen, Y. Wang, H. Tan, S. Su, W. Zhu, Near-infrared emitting pyrazole-bridged binuclear platinum complexes: Synthesis, photophysical and electroluminescent properties in PLEDs, Dyes. Pigm. 128 (2016) 68.

- [24] H. Liu, P. Chen, D. Hu, X. Tang, Y. Pan, H. Zhang, W. Zhang, X. Han, Q. Bai, P. Lu, Y. Ma, Separation of Electrical and Optical Energy Gaps: Selectively Adjusting the Electrical and Optical Properties for a Highly Efficient Blue Emitter, Chem. Eur. J. 20 (2014) 2149.
- [25] R. Kim, S. J. Yoo, E. K. Kim, H. S. Yu, S. C. Shin, S. K. Lee, S. K. Kwon, Y. H. Kim, New limb structured blue light emitting materials for OLEDs, Dyes Pigm. 95 (2012) 384.
- [26] I. Cho, S. H. Kim, J. H. Kim, S. Park, S. Y. Park, Highly efficient and stable deep-blue emitting anthracene-derived molecular glass for versatile types of non-doped OLED applications, J. Mater. Chem. 22 (2012) 123.
- [27] W.C. Chen, Y. Yuan, G. F. Wu, H. X. Wei, J. Ye, M. Chen, F. Lu, Q.X. Tong, F.L. Wong, C. S. Lee, Molecular modification on bisphenanthroimidazole derivative for deep-blue organic electroluminescent material with ambipolar property and high performance, Org. Electron. 17 (2015) 159.
- [28] W. Zhao and F. N. Castellano, Upconverted emission from pyrene and di-tertbutylpyrene using Ir(ppy)₃ as triplet sensitizer, J. Phys. Chem. A, 110 (2006) 11440.
- [29] J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, Upconversion luminescent materials: advances and applications, Chem. Rev. 115 (2015) 395.
- [30] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo,

J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT (Revision A.02), *Gaussian, Inc., Wallingford, CT.* (2009).

- [31] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580.
- [32] A. Wakamiya, T. Taniguchi, S. Yamaguchi, Intramolecular B–N Coordination as a Scaffold for Electron-Transporting Materials: Synthesis and Properties of Boryl-Substituted Thienylthiazoles, Angew. Chem. 45 (2006) 3170.
- [33] R. Kim, S. Lee, K.H. Kim, Y.J. Lee, S.K. Kwon, J.J. Kim, Y.H. Kim, Extremely deep blue and highly efficient non-doped organic light emitting diodes using an asymmetric anthracene derivative with a xylene unit, Chem. Commun. 49 (2013) 4664.
- [34] A. O. Eseola, O. Adepitan, H. Gorls, W. Plass, Electronic/substituents influence on imidazole ring donor-acceptor capacities using 1H-imidazo[4,5-f][1,10]phenanthroline frameworks, New. J. Chem. 36 (2012) 891.
- [35] J. Birks, Photophysics of Aromatics Molecules. Wiley, New York. 1970.
- [36] S. Tang, M.R. Liu, P. Lu, H. Xia, M. Li, Z.Q. Xie, F.Z. Shen, C. Gu, H. Wang, B. Yang, Y.G. Ma, A Molecular Glass for Deep-Blue Organic Light-Emitting Diodes Comprising a 9,9'-Spirobifluorene Core and Peripheral Carbazole Groups, Adv. Funct. Mater. 17 (2007) 2869.
- [37] Z. R. Grabowski, K. Rotkiewicz, W. Rettig, Structural Changes Accompanying Intramolecular Electron Transfer: Focus on Twisted Intramolecular Charge-Transfer States and Structures, Chem. Rev. 103 (2003) 3899.

- [38] Y. Zou, J. H. Zou, T. L. Ye, H. Li, C. L. Yang, H. B. Wu, D. G. Ma, J. G. Qin, Y. Cao, Unexpected Propeller-Like Hexakis(fluoren-2-yl)benzene Cores for Six-Arm Star-Shaped Oligofluorenes: Highly Efficient Deep-Blue Fluorescent Emitters and Good Hole-Transporting Materials, Adv. Funct. Mater. 23 (2013) 1781.
- [39] C. Liu, Q. Fu, Y. Zou, C. L. Yang, D. G. Ma, J. G. Qin, Low Turn-on Voltage, High-Power-Efficiency, Solution-Processed Deep-Blue Organic Light-Emitting Diodes Based on Starburst Oligofluorenes with Diphenylamine End-Capper to Enhance the HOMO Level, Chem. Mater. 26 (2014) 3074.
- [40] E. Lippert, W. Lüder, H. Boos, Advances in Molecular Spectroscopy. (Ed: A. Mangini) Pergamon, Oxford 1962.
- [41] a) Z. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok, Y. Ma, Phenanthro[9,10-*d*]imidazole as a new building block for blue light emitting materials, J. Mater. Chem. 21 (2011) 5451; b) H. Huang, Y. Wang, B. Wang, S. Zhuang, B. Pan, X. Yang, L. Wang, C. Yang, Controllably tunable phenanthroimidazole–carbazole hybrid bipolar host materials for efficient green electrophosphorescent devices, J. Mater. Chem. C. 1 (2013) 5899; c) Z. Gao, Y. Liu, Z. Wang, F. Shen, H. Liu, G. Sun, L. Yao, Y. Lv, P. Lu, Y. Ma, High-Efficiency Violet-Light-Emitting Materials Based on Phenanthro[9,10-*d*]imidazole, Chem. Eur. J. 19 (2013) 2602; d) Z. Wang, Y. Feng, H. Li, Z. Gao, X. Zhang, P. Lu, P. Chen, Y. Ma, S. Liu, Dimeric phenanthroimidazole for blue electroluminescent materials: the effect of substituted position attached to biphenyl center, Phys. Chem. Chem. Phys. 16 (2014) 10837; e) Z. Gao, Z. Wang, T. Shan, Y. Liu, F. Shen, Y. Pan, H. Zhang, X. He, P. Lu, B. Yang, Y. Ma, High-efficiency deep blue fluorescent emitters based on phenanthro[9,10-d]imidazole substituted carbazole and their applications in organic light emitting diodes, Org. Electron. 15 (2014) 2667; f) Z. Gao, G. Cheng, F. Shen, S. Zhang, Y. Zhang, P. Lu, Y. Ma, Highly efficient deep blue

light emitting devices based on triphenylsilane modified phenanthro[9, 10d]imidazole, Laser Photonics Rev. 8 (2014) L6.

- [42] a) V. E. Z. Lippert, Spektroskopische Bestimmung des Dipolmomentes aromatischer Verbindungen im ersten angeregten Singulettzustand, Electrochemistry. 61(1957) 962; b)
 N. Mataga, Y. Kaifu, M. Koizumi, Solvent Effects upon Fluorescence Spectra and the Dipolemoments of Excited Molecules, Chem. Soc. Jpn. 29 (1956) 465.
- [43] C. J. Chiang, A. Kimyonok, M. K. Etherington, G. C. Griffiths, V. Jankus, F. Turksoy, A.P. Monkman, Ultrahigh Efficiency Fluorescent Single and Bi-Layer Organic Light Emitting Diodes: The Key Role of Triplet Fusion, Adv. Funct. Mater. 23 (2013) 739.
- [44] R. L. Martin, Natural transition orbitals, J. Chem. Phys. 118 (2003) 4775.
- [45] a) S. P. Jagtap, S. Mukhopadhyay, V. Coropceanu, G. L. Brizius, J. Bré das, D. M. Collard, Closely Stacked Oligo(phenylene ethynylene)s: Effect of π-Stacking on the Electronic Properties of Conjugated Chromophores, J. Am. Chem. Soc. 134 (2012) 7176;
 b) S. Shirai, S. Iwata, T. Tani, S. Inagaki, Ab Initio Studies of Aromatic Excimers Using Multiconfiguration Quasi-Degenerate Perturbation Theory, J. Phys. Chem. A. 115 (2011) 7687.
- [46] Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki, C. Adachi, Design of Efficient Thermally Activated Delayed Fluorescence Materials for Pure Blue Organic Light Emitting Diodes, J. Am. Chem. Soc. 134 (2012) 14706.
- [47] S. T. Zhang, W. J. Li, L. Yao, Y. Y. Pan, B. Yang, Y. G. Ma, Enhanced proportion of radiative excitons in non-doped electro-fluorescence generated from an imidazole derivative with an orthogonal donor–acceptor structure, Chem. Commun. 49 (2013) 11302.
- [48] a) M. Segal, M. Singh, K. Rivoir, S. Difley, T. V. Voorhis, M. A. Baldo, Extrafluorescent electroluminescence in organic light-emitting devices, Nat. Mater. 6

(2007) 374; b) W. Barford, Theory of singlet exciton yield in light-emitting polymers, Phys. Rev. B. 70 (2004) 205204.

- [49] S. Zhang, L. Yao, Q. Peng, W. Li, Y. Pan, R. Xiao, Y. Gao, C. Gu, Z. Wang, P. Lu, F. Li, S. Su, B. Yang, Y. Ma, Achieving a Significantly Increased Efficiency in Nondoped Pure Blue Fluorescent OLED: A Quasi-Equivalent Hybridized Excited State, Adv. Funct. Mater. 25 (2015) 1755.
- [50] H. Liu, Q. Bai, L. Yao, H. Zhang, H. Xu, S. Zhang, W. Li, Y. Gao, J. Li, P. Lu, H. Wang, B. Yang, Y. Ma, Highly efficient near ultraviolet organic light-emitting diode based on a meta-linked donor-acceptor molecule, Chem.Sci. 6 (2015) 3797.
- [51] Z. Wang, Y. Feng, H. Li, Z. Gao, X. Zhang, P. Lu, P. Chen, Y. Ma, S. Liu, Dimeric Phenanthroimidazole for blue Electroluminencent Materials: The Effect of Substituted Position Attaching to Biphenyl Center, Phys. Chem. Chem. Phys. 16 (2014) 10837.
- [52] W. Li, L. Yao, H. Liu, Z. Wang, S. Zhang, R. Xiao, H. Zhang, P. Lu, B. Yang, Y. Ma, Highly efficient deep-blue OLED with an extraordinarily narrow FHWM of 35 nm and a y coordinate <0.05 based on a fully twisting donor-acceptor molecule, J.Master.Chem.C. 2 (2014) 4733.
- [53] Mei-Fang lin, L. Wang, Wai-Knok Wong, Kwok-Wai Cheah, Hoi-Lam Tam, Meng-Ting Lee, Chin H. Chen, Highly efficient and stable sky blue organic light-emitting devices, Appl. Phys. Lett. 89 (2006) 121913.
- [54] Z. Gao, Y. Liu, Z. Wang, F. Shen, H. Liu, G. Sun, L. Yao, Y. Lv, P. Lu, Y. Ma, High-Efficiency Violet-Light-Emitting Materials Based on Phenanthro[9,10-d]imidazole, Chem. Eur. J. 19 (2013) 2602.
- [55] X. L. Li, X. Ouyang, D. Chen, X. Cai, M. Liu, Z. Ge, Y. Cao, S. J. Su, Highly efficient blue and warm white organic light-emitting diodes with a simplified structure, Nanotechnology. 27 (2016) 124001.

- [56] Y. Zhang, T. W. Ng, F. Lu, Q. X. Tong, S. L. Lai, M. Y. Chan, H. L. Kwong, C. S. Lee, A pyrene-phenanthroimidazole derivative for non-doped blue organic light-emitting devices, Dyes and Pigments 98 (2013) 190.
- [57] A. Fisher, S. Chenais, S. Forget, M. C. Castex, D. Ades, A. Siove, C. Denis, P. Maisse,B. Geffroy, Highly efficient multilayer organic pure- blue-light emitting diodes with substituted carbazoles compounds in the emitting layer, Journal of Physis D: Applied Physics, 39 (2006).
- [58] Y. Zhang, S. L. Lai, Q. X. Tong, M. F. Lo, T. W. Ng, M. Y. Chan, Z. C. Wen, J. He, K. S. Jeff, X. L. Tang, W. M. Liu, C. C. Ko, P. F. Wang, C. S. Lee, High Efficiency Nondoped Deep-Blue Organic Light Emitting Devices Based on Imidazole-π-triphenylamine Derivatives, Chem. Master. 24 (2012) 61.
- [59] F. I. Wu, P. I. Shih, M. C. Yuan, A. K. Dixit, C. F. Shu, Z. M. Chung, E. W. G. Diau, Novel distyrylcarbazole derivatives as hole-transporting blue emitters for electroluminescent devices, J. Mater. Chem. 15 (2005) 4753.
- [60] Y. L. Liao, C. Y. Lin, K. T. Wong, T. H. Hou, W. Y. Hung, A Novel Ambipolar Spirobifluorene Derivative Behaves as an Efficient Blue-Light Emitter in OLEDs, Org. Lett. 9 (2007) 4511.

120 T_d - 428 °C Td - 436 °C $T_g - 154 \ ^{\circ}C$ T_m 100 T_d - 422 °C T_d- 420 °C T_d-404 °C Heat flow (mW/mg) – 300 °C TPA-TPICN -0-Weight (%) 80 $T_g - 150 \circ C T_m - 298 \circ C$ Py-SPICN _ -0-60 \sim -0- $T_g - 142 \ ^\circ C$ Py-TPICN --->-Tm - 296 °C Py-SPICN _ Py-TPICN --> 40 TPA-TPICN ------Tg-130 °C Tm - 256 °C Exo 20 Py-PPICN -4 Tg - 110 °C T_m - 289 °C 0 250 150 200 200 400 600 100 300 Ó Temperature (°C) Temperature (°C)

Figure 1: DSC and TGA graphs of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN.

Figure 2: HOMO and LUMO contour map of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN



θ1 **θ**1 $\theta_{1} - 62.5^{\circ}$ **θ**3 θ2 **θ**₂−7.7° **Py-PPICN** θ₃-98.83° **0**3 θ2 θ3 **θ**1 $\theta_1 - 73.4^{\circ}$ θ₂-3.8° θ2 θ₃-106.2° **Py-TPICN θ**1 **0**3 θ₁-88.6° $\theta_2 - 2.2^{\circ}$ Py-SPICN θ₃-110.6° θ1 **θ**1 **0**3 θ2 θ3 $\theta_1 - 72.62^{\circ}$ $\theta_2 - 26.6^{\circ}$ θ2 TPA TPICN θ₃-40.5° **θ**1 A $\theta_1 - 76.5^{\circ}$ θ2 θ3 θ₂-30.2° θ2 θ₃-39.8° **Cz-TPICN**

Figure 3: The ground state geometries of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN.



Figure 4: (a) Normalized absorption and (b) emission spectra of Py-PPICN, Py-SPICN, TPA-TPICN and Cz-TPICN in dichloromethane and film **Figure 5:** (a) Cyclic voltamogram of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN; (b) The lifetime decay curve of Py-PPICN, Py-TPICN and Py-SPICN; (c) TPA-TPICN and Cz-TPICN and (d) Lippert–Mataga plot of TPA-TPICN and Cz-TPICN in different solvents



Figure 6: a) Energy level of singlet (S) and triplet (T) states of TPA-TPICN and Cz-TPICN; (b) Scheme of exciton decay process after hole and electron recombination in OLEDs of twisting $D-\pi$ -A molecules





Figure 7: Computed natural transition orbital pairs for S₁-S₃ and T₁-T₃of TPA-TPICN and Cz-TPICN [*f*-oscillator strength]



Figure 8: Schematic diagram of hybridization processes of LE and CT states of TPA-TPICN and Cz-TPICN



Figure 9: Energy-level diagram of the materials used for the fabrication of devices.

Figure 10: Electroluminescence performances: (a) Luminance versus Voltage; (b) External quantum efficiency versus Current density; (c) Current efficiency versus Current density and (d) Power efficiency versus Current density of non-doped EL device with Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN as emitter





Scheme 1: Synthetic route of Py-PPICN, Py-SPICN, Py-TPICN, TPA-TPICN, Cz-TPICN and TPA-TPICN

Parameters	Py-PPICN	Py-TPICN	Py-SPICN	TPA-TPICN	Cz-TPICN
$\lambda_{ab}(nm)$ (soln/film)	230, 254, 310/	235, 260, 320/	238, 265, 325/	232, 252, 305/	231, 248, 291/
	260, 320	264, 335	269, 340	251, 312	240,301
$\epsilon (M^{-1} cm^{-1})$	16400	15800	17600	29800	32400
$\lambda_{em}(nm)$ (soln/film)	405/ 420	432/ 440	445/450	410/446	401/425
$\mathrm{T}_d / \mathrm{T}_g / \mathrm{T}_m (^\circ\mathrm{C})$	420/ 110/ 289	404/ 130/ 256	422/ 142/ 296	428/ 150/ 298	436/ 154/ 300
HOMO/LUMO/ Eg (eV)	-5.20/ -2.44/ -2.76	-5.16/ -2.60/ -2.50	-5.10/ -2.54/ -2.56	-5.23/ -2.67/ -2.56	-5.38/ -2.72/ -2.66
Φ (soln/film)	0.45/ 0.42	0.51/ 0.48	0.55/ 0.50	0.62/ 0.60	0.70/ 0.65
τ (ns)	4.2	4.9	5.4	6.1	5.8
k _r /k _{nr} (×10 ⁻⁸ s ⁻¹)	1.07/ 1.31	1.04/ 1.00	1.21/ 0.52	1.02/ 0.62	1.20/ 0.83

Table 1: Optical and thermal properties of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN

Table 2: Dihedral angles (°) in Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-

TPICN

	θ1	θ2	θ3
Py-PPICN	62.50	7.70	98.83
Py-TPICN	73.40	3.80	106.20
Py-SPICN	88.60	2.20	110.60
TPA-TPICN	72.62	26.60	40.50
Cz-TPICN	76.50	30.20	39.80

 θ_1 – Dihedral angle between benzonitrile ring and imidazole ring; θ_2 – Dihedral angle between phenyl/ thiophene/ styryl ring and imidazole ring; θ_3 – Dihedral angle between phenyl/ thiophene/ styryl ring and pyrene/ triphenyl amine/ carbazole ring

Parameters	Py-PPICN	Py-TPICN	Py-SPICN	TPA-TPICN	Cz-TPICN
V1000 (V)	3.4	3.6	3.3	3.1	3.0
L (cd/m ²)	12925	14592	15960	14625	14802
η_{ex} (%)	1.42	1.34	1.48	1.56	1.64
$\eta_c (cd A^{-1})$	3.21	3.00	3.41	3.51	3.65
$\eta_p (lm \; W^{\text{-}1})$	2.50	2.62	2.80	2.89	3.10
EL (nm)	420	440	451	447	427
CIE	(0.15, 0.16)	(0.15, 0.18)	(0.15, 0.15)	(0.16, 0.12)	(0.15, 0.10)
η _{IQE} (%)	-	-	-	7.8	8.2
η _s (%)	-	-	-	13.0	12.6

Table 3: Device performances of Py-PPICN, Py-TPICN, Py-SPICN, TPA-TPICN and Cz-TPICN

 $\begin{array}{l} \eta_c \ \ - \ \ luminous \ \ efficiency; \ \eta_p \ \ - \ \ power \ \ efficiency; \ \eta_{ex} \ \ - \ \ external \ \ quantum \ \ efficiency; \\ EL \ \ - \ \ electroluminescence; \ \eta_{IQE} \ \ - \ \ maximum \ internal \ \ quantum \ \ efficiency; \ (\eta_{IQE} = \eta_{EQE} / \eta_{out}), \ \eta_s \ \ - \ \ light \ out \ \ coupling \ \ efficiency \ (\eta_{IQE} / \eta_{PL}). \end{array}$