New Pyrene Cored Small Organic Molecule with Flexible Alkyl Spacer: The Potential Solution Processable Blue Emitter with Bright Photoluminescence

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A new pyrene cored small organic molecule viz., 1,3,6,8-tetrakis(4-((5-(9H-carbazol-9-yl)pentyl)oxy)phenyl)pyrene (PY-II) was designed and synthesized. The carbazole moiety with alkyl spacer was introduced at 1, 3, 6 and 8 positions of pyrene core to improve the charge transport properties and solution processability. PY-II exhibited excellent solubility in common organic solvents and high thermal stability up to 345 °C. The photoluminescence quantum yield (PLQY) of **PY-II** in solution was found to be 0.9 with bright blue emission near 450 nm which is just appropriate to human eye. The solution processed non-doped OLED device fabricated using PY-II as an emissive layer afforded a pure blue emission with CIE coordinates of 0.16 and 0.16, the power efficiency of 0.17 lm W⁻¹, maximum current efficiency of 0.41 cd/A and maximum brightness of 202 cdm⁻².

Introduction

Over the past two decades, organic light emitting diodes (OLEDs) have attracted great attention because of their applications in flat panel displays and solid-state lighting devices.¹⁻⁵ Generally, small molecule organic light emitting diodes (SMOLEDs) are fabricated by high-vacuum thermal evaporation whereas polymer light emitting diodes (PLEDs) are fabricated by the solution processing method. Vacuum evaporation results in complicated architectures, is expensive and is not well suited for large area fabrication.^{6,7} On the other hand, solution processing is an attractive method with low cost and large area manufacturability.⁸⁻¹¹ To date, both small molecules and polymers have been extensively used as emitting materials in OLEDs.¹¹⁻¹⁴ Recently, OLEDs based on organic and organometallic compounds have drawn intense interest due to their inherent features such as excellent solution processability, tunable emission properties, thin film forming ability and high chemical and thermal stability. A variety of solution processable fluorescent and phosphorescent light emitting materials have been reported to date.¹⁴⁻¹⁸

Among the various fluorescent chromophores used for OLEDs, pyrene stands out as a promising chromophore because

of its strong emission efficiency and high charge carrier mobility.¹⁹⁻²² These features make pyrene a potential candidate to develop an interesting class of materials for OLEDs. However, supramolecular π - π stacking between pyrene cores in the solid state leads to the red shift and fluorescence quenching of the emission.^{23,24} To overcome these problems, rigid and bulky groups with alkyl chains were introduced at the periphery of pyrene core which prevent the intermolecular aggregation and lead to enhanced emission efficiency.²⁵ A number of light emitting materials based on pyrene have been reported in the literature.²⁶⁻²⁹ Recently, we reported carbazole and phenothiazine containing solution processable blue and green emitting 1, 3, 6, 8-tetrasubstituted pyrene derivatives.²⁷ Pyrene has been successfully utilized for synthesis of materials with pure blue and green emission.³⁰⁻³² Blue light-emitting materials can facilitate white light emission in the presence of suitable dopants.³³⁻³⁶ Thus, it is important to develop new classes of blue emitting materials with good solution processability and high fluorescence efficiency. It is reported that moieties with charge transporting ability and aliphatic chain linkers offer several advantages such as enhancement in the solubility, facilitated charge transport and reduction of intermolecular interaction between the emissive cores.³⁷⁻⁴¹ Such molecules provide a pathway to reduce or eliminate aggregation induced fluorescence quenching by the site isolation effect.

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Fig. 1 Chemical structure of **PY-II** (a), emission under a UV-vis lamp using **PY-II** in solution (b) & spin coated thin film of **PY-II** deposited on quartz plate @ 1500 RPM, 30s using 0.5 mM chloroform solution (c).

According to the above considerations, herein, we report a new pyrene cored solution processable blue light emitting material for OLED devices. The carbazole moiety with alkyl spacer was introduced at 1, 3, 6, 8-positions of the pyrene core. Carbazole was employed due to its high hole transporting and energy harvesting ability,⁴²⁻⁴⁶ and its property to enhance the emission of the core.^{37,41,47} The flexible alkyl chain was introduced to further improve the solution processability and glass-like properties.⁷ The OLED device fabricated using **PY-II** (Fig. 1) as an emitting material showed blue emission with a maximum brightness of 202 cd m^{-2} and a maximum current efficiency of 0.41 cd/A .

Experimental

Chemicals and Characterizations

All the chemicals and solvents were purchased from Sigma-Aldrich and were used without further purification. All the reactions were carried out using a round bottom flask or a Schlenk tube in an argon or nitrogen atmosphere in anhydrous solvents. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker AC spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C . Matrix assisted laser desorption/ionization time-of flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix. UV-vis absorbance and photoluminescence (PL) spectra were recorded on a Jasco V-570, and a Cary Eclipse Fluorescence spectrometer, respectively, using chloroform as a solvent. Thermogravimetric and DSC analyses were performed on PerkinElmer STA 6000 and TA Instrument DSC Q10, respectively at a heating rate of 10 $^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The cyclic voltammogram was recorded on Autolab using conventional three-electrode assembly with a Pt wire as a working electrode, a Pt foil as a counter electrode and Ag/AgCl as a reference electrode. The cyclic voltammetry was carried out in freshly distilled dichloromethane (DCM) using 0.1M tetrabutylammonium hexafluorophosphate (TBAPF_6) as supporting electrolyte and a scan rate of 50 mV sec^{-1} was used. The cyclic voltammogram was calibrated with Fc/Fc^+ redox couple. The HOMO energy level of newly synthesized

molecule **PY-II** was calculated by photoelectron spectroscopy in air (PESA) using a spin coated thin film of **PY-II** on the ITO coated glass substrate. The surface of **PY-II** thin film was irradiated with UV energy that emits photoelectrons of certain energy level known as photoelectron work function. The photoelectron output is plotted with horizontal X-axis as the UV energy applied and the vertical Y-axis as the standardized photoelectron yield ratio, the result is a line with a specific slope of degree (Y/eV). The HOMO value of **PY-II** was calculated from the onset energy level recorded in PESA. Solution and thin film (solid state) photoluminescence quantum yield (PLQY) measurements were carried out with an Absolute PL Quantum Yield Spectrometer (Hamamatsu, C11347) using an integrating sphere equipped with a multichannel spectrometer.⁴⁸ The roughness measurement was conducted by atomic force microscopy (AFM). **PY-II** solution prepared in chloroform was spin-coated on an ITO substrate. It was baked at 70 $^\circ\text{C}$ for 20 min. The scan dimension was typically set as 5 x 5 μm .

Synthesis of 9-(5-bromopentyl)-9H-carbazole (2)

Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a dropping funnel were placed carbazole **1** (2 g, 11.96 mmol), KOH (0.671 g, 11.96 mmol) and DMF (40 mL). The reaction mixture was stirred at room temperature for 1 h. 1,5-Dibromopentane (8.25 g, 35.88 mmol) was added dropwise into the reaction mixture at 0 $^\circ\text{C}$. After the addition, the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (100 mL). The organic layer was washed with water, brine solution, and again with water. The organic layer was dried over anhydrous sodium sulfate and filtered. Removal of the solvent on a rotary evaporator yielded a crude product which was purified by column chromatography using petroleum ether: dichloromethane (9:1, v/v) as an eluent to give compound **2** as a white powder. (2.95 g, yield 78%). ^1H NMR (400 MHz, CDCl_3) δ = 8.12 (d, J = 7.3 Hz, 2 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.41 (d, J = 7.9 Hz, 2 H), 7.31 - 7.19 (m, 2 H), 4.34 (t, J = 7.0 Hz, 2 H), 3.37 (t, J = 6.7 Hz, 2 H), 2.00 - 1.82 (m, 4 H), 1.62 - 1.46 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ = 140.27, 125.61, 122.80, 120.34, 118.80, 108.51, 42.72, 33.28, 32.40, 28.11, 25.83.

Synthesis of 9-(5-(4-iodophenoxy)pentyl)-9H-carbazole (3)

Into a 100 mL round bottom flask equipped with a magnetic stirring bar and a dropping funnel were placed 4-iodophenol (2 g, 9.09 mmol), KOH (36.36 mmol) and DMSO (30 mL). After stirring for 10 minutes, the solution of 9-(5-bromopentyl)-9H-carbazole (3.16 g, 10 mmol) (**2**) in DMSO (20 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was poured into water (50 mL) and extracted with dichloromethane (100 mL). The organic layer was separated and washed with water, brine solution and again with water. The organic layer was dried over anhydrous sodium sulfate and filtered. Removal of solvent on a rotary evaporator yielded a crude product which was purified by column chromatography using petroleum ether: dichloromethane (8:2, v/v) as an eluent to give compound **3** as colorless crystals. (3.72 g, yield 82%). ¹H NMR (400 MHz, CDCl₃) δ = 8.14 (d, *J* = 7.78 Hz, 2H), 7.58-7.45 (m, 4H), 7.44-7.36 (m, 2H), 7.27 (t, *J* = 7.33 Hz, 2H), 6.67-6.55 (m, 2H), 4.33 (t, *J* = 7.10 Hz, 2H), 3.84 (t, *J* = 6.18 Hz, 2H), 2.02-1.88 (m, 2H), 1.84-1.72 (m, 2H), 1.59-1.47 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 158.75, 140.30, 138.09, 125.59, 122.77, 120.33, 118.76, 116.83, 108.55, 82.53, 67.59, 42.81, 28.89, 28.71, 23.77.

Synthesis of 9-(5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)pentyl)-9H-carbazole (4)

Into a 50 mL Schlenk tube were added 9-(5-(4-iodophenoxy)pentyl)-9H-carbazole (**3**) (1 g, 2.20 mmol), bis(pinacolato)diboron (0.669 g, 2.60 mmol), PdCl₂(dppf) (161 mg, 0.2 mmol) and potassium acetate (646 mg, 6.60 mmol) under argon flow and then the tube was evacuated for half an hour. Then, under an argon flow, anhydrous dioxane (10 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 1 h and then at 80 °C for 24 h. The reaction was quenched by addition of ice-cold water (100 mL) and extracted with dichloromethane (200 mL). The combined organic layers were washed with water, brine solution and again with water. The organic layer was dried over anhydrous sodium sulfate and filtered. Removal of the solvent on a rotary evaporator yielded a crude product, which was chromatographed on neutral alumina using 2% ethyl acetate in petroleum ether as an eluent to give compound **4** as a white solid (640 mg, yield 64%). ¹H NMR (400 MHz, CDCl₃) δ = 8.11 (d, *J* = 7.71 Hz, 2H), 7.75 (d, *J* = 8.46 Hz, 2H), 7.52-7.35 (m, 4H), 7.29-7.18 (m, 2H), 6.85 (d, *J* = 8.59 Hz, 2H), 4.31 (t, *J* = 6.95 Hz, 2H), 3.91 (t, *J* = 6.32 Hz, 2H), 2.04-1.87 (m, 2H), 1.85-1.70 (m, 2H), 1.68-1.50 (m, 2H), 1.34 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ = 161.52, 140.33, 136.47, 125.59, 122.78, 120.32, 118.75, 113.80, 108.57, 83.49, 67.30, 42.85, 28.97, 28.73, 24.82, 23.82.

Synthesis of 1,3,6,8-tetrakis(4-((5-(9H-carbazol-9-yl)pentyl)oxy)phenyl)pyrene (PY-II)

Into a 50 mL Schlenk tube were placed 1,3,6,8-tetrabromopyrene (0.1 g, 0.19 mmol), 9-(5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)pentyl)-9H-carbazole (0.528 g, 1.16 mmol), 2M K₂CO₃ (2 mL) and Pd(PPh₃)₄ (22 mg, 0.019 mmol) under argon flow. The tube

was evacuated and refilled with argon three times and then toluene (10 mL) was added into the flask. The reaction mixture was stirred at 80 °C for 48 h and then extracted with dichloromethane (3x50 mL). The combined organic layer was washed with water, brine solution and again with water. The organic layer was dried over sodium sulfate and filtered. Removal of the solvent on a rotary evaporator yielded a crude product, which was purified by column chromatography using petroleum ether: dichloromethane (6:4, v/v) as an eluent to give title compound **PY-II** as a yellow solid (181 mg, yield 62%). ¹H NMR (400 MHz, CDCl₃) δ = 8.22 - 8.04 (m, 12 H), 7.95 (s, 2 H), 7.58 (d, *J* = 7.9 Hz, 8 H), 7.53 - 7.42 (m, 16 H), 7.24 (d, *J* = 7.3 Hz, 8 H), 7.04 (d, *J* = 7.9 Hz, 8 H), 4.39 (t, *J* = 6.7 Hz, 8 H), 4.04 (t, *J* = 5.8 Hz, 8 H), 2.10 - 1.97 (m, 8 H), 1.96 - 1.84 (m, 8 H), 1.71 - 1.60 (m, 8 H). ¹³C NMR (100 MHz, CDCl₃) δ = 158.4, 140.4, 136.7, 133.5, 131.7, 129.6, 128.0, 126.1, 125.6, 125.1, 122.8, 120.4, 118.8, 114.4, 108.6, 67.7, 42.9, 29.1, 28.8, 23.9. MALDI-TOF: Calculated 1510.7275, found 1511.4016.

OLED Device Fabrication and Characterization

OLED devices were fabricated using PY-II active emitting layer for evaluating the electroluminescent (EL) performance. The OLED device configuration glass/ITO/PEDOT: PSS/PY-II/TPBi/LiF/Al was used. Patterned ITO glass substrates were routinely cleaned, blown dry by nitrogen gas and then treated with ultra-violet ozone. The filtered poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) solution was spin-coated on the patterned ITO glass substrates and baked at 140 °C for 20 min. Then PY-II solution prepared in chloroform was spin-coated on PEDOT: PSS coated ITO glass substrates and baked at 70 °C for 20 min. All the spin-coat processes were performed in nitrogen glove box environment. PY-II coated substrates were then loaded into a thermal evaporation chamber at a vacuum of 2x10⁻⁶ Torr. The layers of 20 nm of 2, 2', 2''-(1, 3, 5-benzinetriyl)-tris (1-phenyl-1H-benzimidazole) (TPBi), 1 nm of lithium fluoride (LiF) and 200 nm of aluminium (Al) were coated on the substrates in that sequence. The voltage-current-brightness (I-V-B) characteristics, the C.I.E. coordinates, the EL emission spectra were measured by a Spectra PR650 CCD camera with a computer controlled power supply. The current and power efficiencies were calculated from I-V-B data of the devices.

Results and Discussion

Initially, commercially available carbazole was converted to 9-(5-bromopentyl)-9H-carbazole (**2**) *via* alkylation reaction with excess 1,5-dibromopentane. The compound **2** was subsequently reacted with 4-iodophenol to afford 9-(5-(4-iodophenoxy)pentyl)-9H-carbazole (**3**). The transformation of compound **3** to the boronic ester analog 9-(5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)pentyl)-9H-carbazole (**4**) was carried out *via* Miyaura borylation reaction. The target compound 1,3,6,8-tetrakis(4-((5-(9H-carbazol-9-yl)pentyl)oxy)phenyl)pyrene (**PY-II**) was prepared *via* the classical Suzuki coupling using 1,3,6,8-tetrabromopyrene and

monoboronic ester analogue **4**. The synthesis of **PY-II** is depicted in Scheme 1. **PY-II** was readily soluble in common organic solvents such as dichloromethane, chloroform, toluene and tetrahydrofuran at room temperature. The chemical structure of **PY-II** and intermediate derivatives were confirmed by ^1H NMR, ^{13}C NMR and MALDI-TOF spectroscopy (see ESI† for further details). The thermal properties of **PY-II** were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA and DSC curves are shown in ESI.†

Scheme 1 Synthesis of **PY-II**. Reagents and conditions: i) 1,5-dibromopentane, KOH, DMF, rt, 12 h; ii) 4-iodophenol, KOH, DMSO, rt, 24 h; iii) bis(pinacolato)diboron, $\text{PdCl}_2(\text{dppf})$, AcOK, 1,4-dioxane, 80 °C, 24 h; iv) 1,3,6,8-tetrabromopyrene, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , aliquat, toluene, 80 °C, 48 h.

PY-II showed high thermal stability with initial decomposition at 345 °C and 5 % weight loss at 435 °C. In DSC analysis **PY-II** exhibited a sharp melting peak at 215 °C during the first heating scan. However, after cooling and reheating of sample during the second heating scan, it demonstrated the molecular glass behaviour with glass transition temperature (T_g) at 82 °C. Further heating above T_g did not result in any other thermal transitions indicating the formation of stable amorphous glass.

Density Functional Theory (DFT)⁴⁹ calculations were performed to compute molecular structures, the energies of the frontier orbitals and their localization as well as absorption and photoluminescence spectra. The calculations were carried out using B3LYP⁵⁰ (for frontier orbital energies and optical properties) and CAM-B3LYP⁵¹ (for the oxidation potential) with the LANL2DZ basic set. The absorption and PL spectra were computed with time dependent DFT (TD-DFT) considering the lowest six excited states.⁵² The PL spectrum was computed by optimizing the first excited state. The calculations were performed with the polarizable continuum model (PCM) of the chloroform solvent.⁵³ The calculations were performed using Gaussian 09.⁵⁴ The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular) of **PY-II** are shown in Fig. 2.

Fig. 2 Distributions of HOMO and LUMO of **PY-II** obtained with DFT.

The HOMO and LUMO are centered on the pyrene core. The HOMO is only slightly more delocalized than LUMO and has appreciable amplitude on the oxyphenylene moieties, while the LUMO is localized on the central pyrene core and partially on the oxyphenylene moieties. The theoretically predicted HOMO and LUMO values are -5.18 eV and -1.96 eV, respectively. The HOMO-LUMO bandgap for **PY-II** was calculated to be 3.22 eV. The absorption and PL peak maximum of **PY-II** computed by B3LYP are 424 nm and 523 nm, respectively. The absorption and PL spectra are shown in ESI. † It was previously shown that a functional with a significant fraction of exact exchange is required to accurately estimate the oxidation potential.^{55,56} The oxidation potential was therefore estimated using the range-separated hybrid functional CAM-B3LYP from the difference in energies of (respectively optimized) neutral and cationic states,^{55,56} giving the value of 5.44 eV, which is in good agreement with the experimental value (see below).

The optical properties of **PY-II** were characterized by UV-vis absorption and photoluminescence spectroscopy. The absorption spectra of **PY-II** in chloroform solution and in solid state are shown in Fig. 3 (upper). The absorption in the range 275 nm to 500 nm clearly indicated wide band gap nature of **PY-II**. In solution, **PY-II** exhibited absorption peaks at 297 nm and 394 nm which are originated from π - π^* transition of carbazole moieties and pyrene core, respectively.

Fig. 3 Absorption (top) and Photoluminescence (bottom) spectra of **PY-II** in solution and solid state

When compared with the absorbance peak of molecular pyrene (338 nm), the absorption peak at 394 nm exhibited red shift of 56 nm, which could be attributed to extended conjugation length between pyrene core and the attached oxyphenylene moiety. The absorption spectrum in solid state was nearly identical to that in solution with absorption peaks at 298 nm and 408 nm. The optical band gap calculated from absorption onset value from the thin film spectrum was found to be 2.76 eV. This higher band gap value of **PY-II** is a clear indication of a blue emitter. The photoluminescence (PL) spectra of **PY-II** in both solution and solid state are shown in Fig. 3 (bottom panel). The emission peaks at 434 nm and 450 nm were observed in solution and thin film of **PY-II**, respectively. The thin film emission at 450 nm is the most suitable blue emission colour for human eye. The shape of the emission spectrum in thin film is almost similar to that in solution with slight red shift of 16

nm. This result clearly indicated little intermolecular interaction between the emissive cores which could be attributed to the encapsulation effect of the alkyl separated carbazole moiety.

Fig. 4 Transient PL decay curves of **PY-II** in solution (a) and thin film (b)

The PL quantum yield (PLQY) of **PY-II** in chloroform solution and thin film were measured by using integrating sphere technique after argon gas bubbling for the solution sample and under ambient atmosphere for film sample. In solution **PY-II** exhibited a very high PLQY of almost 0.9. In our samples, there are two fluorophores namely pyrene (Py) and carbazole (Ca). Absorption band of Ca is located higher than that of Py. If there is no energy transfer occurs between Py and Ca fluorophores then they emit fluorescence independently. In such scenario, CA moiety can be preferably excited by shorter wavelength light and Py moiety can be preferably excited by longer wavelength light. If PLQY of pyrene moiety is higher than that of carbazole moiety, PLQY at shorter wavelength excitation is smaller than PLQY at longer wavelength excitation because fraction of excited Py (or Ca) moiety is different. This is not the case in our present study that's why PLQY values were not sensitive to the excitation wavelength between 300 nm and 400 nm. In this excitation wavelength range, absorption due to pyrene and carbazole moieties coexists. Since absorption due to pyrene moiety is located at longer wavelength range, fluorescence spectra shown in Fig. 3 is assigned to pyrene fluorescence. Accordingly, change of PLQY and spectral shape are expected to be observed, if carbazole moiety is excited preferably at shorter wavelength range. As mentioned above, no change of PLQY and spectral

shape was observed in this excitation wavelength range. This clearly shows that energy transfer from the excited carbazole moiety to the pyrene part occurs efficiently and subsequently fluorescence emission occurs with high PLQY. In other words, all excitation energy obtained by light absorption is converted to the excitation energy of Py. Thus, PLQY value is determined by PLQY of pyrene moiety. We also observed spectral shape is not sensitive to excitation wavelength. This again indicates the presence of energy transfer from CA to Py because only Py gives fluorescence. However, the PLQY value in thin film was smaller than that in solution with the value of 0.33, suggesting some deactivation processes are induced. For further insight into excited-state relaxation processes, time-resolved PL decay measurements were carried out in chloroform solution and thin film (Fig 4). In solution, **PY-II** exhibited a simple exponential decay with a fluorescence lifetime (τ) of 1.75 ns, while in thin film double exponential decay profile was observed with a lifetime of 0.5 ns (93%) and 2.8 ns (7%) for fast and slow components, respectively. The fast component spectrum of film was similar to that in solution. This suggests that the fast component is originated from the pyrene moiety and quenched through some decay process, judging from the shorter lifetime. After decay of the fast component fluorescence, the slow component fluorescence was observed (Fig. S12) at longer wavelength range.

Fig. 5 Photoelectron spectroscopy in air (PESA) analysis of **PY-II** in thin film.

This is a possible reason for the slight difference of spectral shape between the solution and the film, which suggests that energy transfer takes place from the pyrene moiety to some defect site, presumably to the aggregates of carbazole moieties. The high photoluminescence in solution of **PY-II** is an attractive signature to use this fluorescent material with high brightness not only in photonic applications but also in other applications such as bioimaging or chemical sensing where high solution quantum yield is desired.

The HOMO level of **PY-II** was characterized by photoelectron spectroscopy in air (PESA) as shown in Fig. 5. Thin film of **PY-II** was spin coated on an ITO substrate, which was used for determination of ionization potential. The

photoelectron yield ratio was measured with respect to applied UV-energy. The onset value calculated from this graph gave HOMO value of -5.71 eV. Additionally, the HOMO level of **PY-II** was investigated using cyclic voltammetry and voltammogram is shown in ESI.† The HOMO level calculated from onset oxidation potential (-0.84 eV) was found to be -5.64 eV, which is in good agreement with the HOMO level (-5.71 eV) calculated by PESA. Such a low HOMO value could be attributed to the presence of a non-conjugated aliphatic spacer in the structure, which is important for obtaining air stable organic electronic devices. The device configuration using compound **PY-II** as an active emissive layer is shown in Figure 6 with ITO/PEDOT:PSS(50nm)/**PY-II** (35 nm)/TPBi (20 nm)/LiF (1 nm)/Al (200 nm) device architecture. ITO coated glass and LiF/Al act as anode and cathode, respectively, whereas TPBi is an electron transporting layer.

Fig. 6 The OLED device architecture using **PY-II**.

Table 1. EL performance summary of **PY-II** based OLED devices.

Turn on voltage (V) @1cd/m ²	Current efficiency (Cd/A)	Power efficiency (lm/W)	CIE	EL peak (nm)	Max. Brightness (cd/m ²)
4.5	0.41	0.17	(0.16, 0.16)	445, 470	202

When a potential is applied, holes are injected from the anode and electrons are injected from the cathode, respectively. Due to recombination of holes and electrons in the active emissive layer, blue photon emission was observed in the OLED devices. The obtained OLED device performance parameters such as turn on voltage, current efficiency, power efficiency, CIE coordinates, electroluminescent peak and maximum brightness and their values are given in Table 1. The observed electroluminescence (EL) spectrum is shown in Fig. 7 (bottom panel). **PY-II** device exhibited an EL maxima of 445 nm and 470 nm emission peaks in visible blue region with a full wave half maximum (FWHM) of 70 nm and CIE coordinates of 0.16 and 0.16. We have noticed that **PY-II** exhibits different EL

spectrum than PL spectrum. We measured the EL spectra of the **PY-II** device from 5-11V, all spectra contain two emission peaks, one at 450 and other at 470 nm. The difference between the PL and EL spectra is attributed to the voltage effect and this can be clearly seen in the applied voltage-EL graph (See S13). **PY-II** device showed a turn on voltage (V_{on}), maximum current efficiency (CE_{max}), maximum power efficiency (PE_{max}), maximum brightness (B_{max}) of 4.5 V, 0.41 cd/A, 0.17 lm/W and 202 cd/m², respectively. The details of j-V-B, CE and PE characteristics of **PY-II** device are shown in Fig. 7 (top panel) and ESI,[†] respectively. As the voltage was increased from 4.5 V to 7 V and 8.5 V, the CE and PE of **PY-II** device increased rapidly to CE_{max} and PE_{max} of 0.41 cd/A and 0.17 lm/W, respectively. As the drive voltage was further increased, CE and PE curves of **PY-II** device typically roll-off. However, CE and PE of **PY-II** device still remained at higher than one-half of the CE_{max} and PE_{max} even as the drive voltage was further increased beyond 10 V. The stable blue colour output additionally proves that **PY-II** has high prospective to be a blue emitter in OLED applications. The turn on voltage of 4.5 V also makes **PY-II** based OLED device energy efficient. The detailed summary of OLED device is shown in Table 1.

The morphological behaviour of the **PY-II** active layer thin film was characterized by AFM as shown in ESI.[†] The measured root mean square (RMS) roughness of film samples is 3.46 nm. The pristine ITO coated glass showed surface roughness with an RMS of 3.25 nm. **PY-II** exhibited a low roughness value, which is desirable for transportation of holes and electrons in the recombination zone.

Fig. 7 Current- voltage-brightness characteristics (top) and electroluminescence spectrum of **PY-II** (bottom)

Conclusions

In summary, we demonstrated the design strategy and synthesis of a new pyrene cored small organic molecule, namely, **PY-II** containing carbazole moiety with alkyl spacer for solution processable OLEDs. **PY-II** exhibited excellent solution processability and high thermal stability. **PY-II** showed wide absorption in the range 275 nm to 500 nm with an optical band gap of 2.76 eV. The PLQY of **PY-II** was found to be 0.90 and 0.33 in solution and solid state, respectively. The HOMO level calculated using PESA was found to be -5.71 eV. The solution processed non-doped OLED device using **PY-II** as EML exhibited turn on voltage of 4.5 V, blue emission with EL peaks at 445 nm and 470 nm, a maximum brightness of 202 cd/m² and a power efficiency of 0.17 lm/W. These results support that this class of functional materials hold a high potential for future cost effective and efficient light emitting materials for OLED devices. We believe that further improvements with introduction of a larger number of conjugated moieties on the pyrene core would greatly improve the performance of molecular and device structure. The higher PLQY and higher brightness in solution are important attributes for bioimaging and sensor applications where **PY-II** in solution can be used. Overall, the present study pinpoints a useful strategy to design new solution processable pyrene-based materials as blue emitters with bright photoluminescence.

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