



# A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrene-based green and blue emitters with 4-*tert*-butylphenyl and arylamine attachments



Ran Zhang, Yun Zhao, Tengfei Zhang, Lu Xu, Zhonghai Ni\*

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, People's Republic of China

## ARTICLE INFO

### Article history:

Received 18 January 2016

Received in revised form

25 February 2016

Accepted 10 March 2016

Available online 14 March 2016

### Keywords:

Pyrene-based

Symmetrical

Tetrasubstituted

Synthesis

Property

OLED

## ABSTRACT

A series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrene-based derivatives (**4a–4c**) with two 4-*tert*-butylphenyl segments at 1,8-positions and two hole-transporting arylamine attachments at 3,6-sites of pyrene core were designed and synthesized based on stepwise synthetic strategy. These compounds were structurally characterized and their photoelectric properties were investigated by spectroscopy, electrochemical and theoretical studies. The results show that the incorporation of different arylamine units into pyrene core can tune the electronic structures of the compounds, and polysubstituted configuration of pyrene can effectively suppress the intermolecular  $\pi$ – $\pi$  interactions and consequently leads to relatively high absolute fluorescence quantum efficiencies. These compounds exhibit high thermal stability and can form morphologically stable amorphous thin films with glass transition temperature in the range of 156–189 °C. Solution-processed non-doped green and blue organic light-emitting diodes with maximum luminance efficiencies 4.14 cd A<sup>-1</sup> and 2.41 cd A<sup>-1</sup> were achieved for **4b** and **4c**, respectively.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive attention over the last two decades because of their potential applications in flat panel displays and general lightings [1–3]. The main research focuses in this field include the design and synthesis of new materials with excellent photoelectric properties and the efficient device fabrication techniques [4–7]. Among the many famous candidate materials for OLEDs, polyaromatic pyrene has been paid everlasting attention due to its pure blue fluorescence with high quantum yield, long fluorescence lifetime, excellent thermal stability, and high charge carrier mobility [8–10]. However, pyrene and its some derivatives tend to form excimers in solid state through  $\pi$ – $\pi$  stacking due to the flat structure of pyrene core, giving rise to the red-shifted emission, the decrease of fluorescence quantum yield and the degrade of colour purity, which brings a big obstacle for the solid state applications of such pyrene-based compounds. To obtain excellent pyrene-based OLED materials, the most effective strategies involve the control of the

supramolecular structures and the optimization of functional units through the introduction of bulky peripheral attachments into the suitable positions of pyrene core [11–14]. Indeed, a larger number of pyrene-based compounds with interesting photoelectric properties and various molecular architectures and supramolecular structures have been designed and synthesized up to date [15–17]. Some of them have been exploited as efficient hole-transporting or host emitting materials for high performance OLEDs [18–22]. However, the reported pyrene derivatives are almost 1-substituted pyrenes, 1,6-disubstituted and 1,3,6,8-tetrasubstituted pyrenes with the same group, and some non-symmetrically 1,3,6,8-tetrasubstituted pyrenes with different peripheral segments at 1,6- and 3,8-positions of pyrene ring [23,24]. The purely 1,8-disubstituted pyrenes are very limited due to the synthetic challenge [8]. Naturally, to the best of our knowledge, there is still no report on short axially symmetrically 1,3,6,8-tetrasubstituted pyrenes with different peripheral attachments at 1,8- and 3,6-positions of pyrene core, which can not only offer more novel compounds but also provide one effective strategy for molecular electronic tuning, interface control and optimization of film morphologies of pyrene-based photoelectric materials.

Recently, we designed and synthesized three novel short axially

\* Corresponding author.

E-mail address: [nizhonghai@cumt.edu.cn](mailto:nizhonghai@cumt.edu.cn) (Z. Ni).

symmetrically 1,3,6,8-tetrasubstituted pyrenes with two different functional attachments at 1,8- and 3,6-positions, respectively, through the stepwise derivatization and functional transformation strategy using pyrene as the precursor (Scheme 1). The introduction of 4-*tert*-butylphenyl groups into the 1,8-positions of pyrene ring can be beneficial to the separation of pure 1,8-disubstituted pyrenes and their solution-processed property. The incorporation of different arylamines is to improve the hole-injection and transporting properties of the emitting materials. Herein, we report the design, synthesis and photoelectrical properties of the new series of short axially symmetrically 1,3,6,8-tetrasubstituted pyrenes with two different functional attachments (**4a–4c**). In addition, solution-processed OLEDs with two representative compounds as non-doped emitting layer were investigated.

## 2. Experimental section

### 2.1. General

Dichloromethane was distilled from calcium hydride. All chemicals used were purchased from commercial sources and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on a Bruker-400 MHz or Bruker-600 MHz spectrometer in  $\text{CDCl}_3$  solution with TMS as an internal standard. Mass spectra were obtained on a Bruker Ultraflex extreme MALDI TOF/TOF mass spectrometer. Elemental analyses (C, H, N) of the dried solid samples were carried out using an Elementary Vario El analyser. UV–Vis spectra were recorded on Shimadzu UV-3600 with a UV–VIS–NIR spectrophotometer. Emission spectra were performed by a HITACHI fluorescence spectrometer (F-4600). The absolute fluorescence quantum yields ( $\Phi_F$ ) were determined by FM-4P-TCSPC Transient State Fluorescence Spectrometer using an integrating sphere for dilute dichloromethane solution and thin films which obtained by drop-casting on quartz plate. Cyclic voltammetry experiments were

performed with a CHI660A electrochemical work station. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum auxiliary electrode and a calomel reference electrode. The solvent in all experiments was dry dichloromethane and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. The glass-transition temperatures ( $T_g$ ) of the compounds were determined with differential scanning calorimetry (DSC) under a nitrogen atmosphere by using a DSC6000 (PerkinElmer). Samples were heated to 400 °C at a rate of 10 °C  $\text{min}^{-1}$  and cooled at 10 °C  $\text{min}^{-1}$  then heated again under the same heating conditions as used in the initial heating process. Decomposition temperature ( $T_d$ ) were determined with thermogravimetric analysis (TGA) under a nitrogen atmosphere by using a DTG-60AH (Shimadzu). Samples were heated to 800 °C at a rate of 10 °C  $\text{min}^{-1}$ . The ground state geometries of all molecules were fully optimized using density functional theory (DFT) at the B3LYP/6-31G (d, p) level, as implemented in Gaussian 09W software package [25]. The electronic transitions were calculated using the time-dependent DFT (B3LYP) theory and the 6-31G (d, p) basis set.

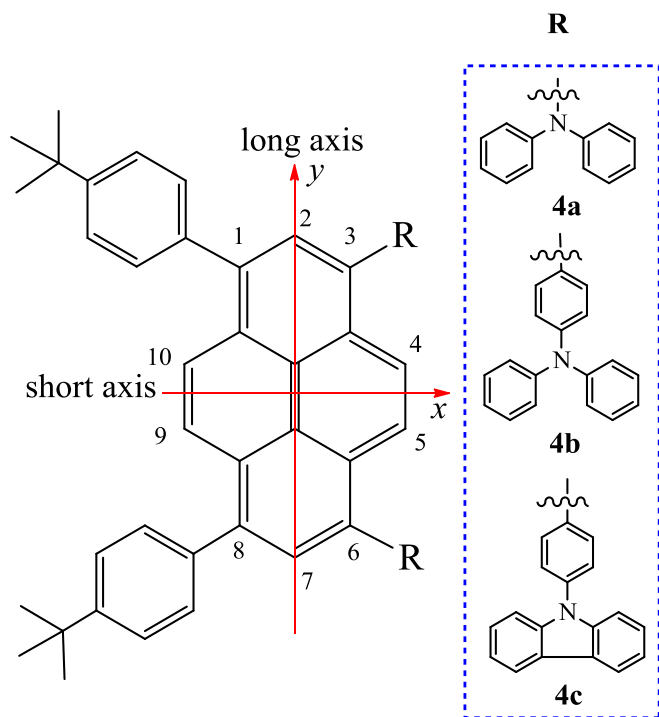
### 2.2. OLED fabrication and performance evaluation

Poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron PAI 4083) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) were purchased from Heraeus Precious Metals GmbH Co. KG and Luminescence Technology Corp., respectively. The OLEDs have a structure of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/**4b** or **4c** (40 nm and 50 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (150 nm) [26]. For the device fabrication, a 40 nm-thick PEDOT:PSS layer was spin-coated from an aqueous dispersion of PEDOT:PSS onto the pre-cleaned ITO substrate and then annealed at 120 °C for 30 min in air condition. Subsequently, the EML was spin-coated with two different thickness from its fresh tetrahydrofuran solution at a spin speed of 1200 rpm or 1500 rpm and then annealed at 100 °C for 30 min to remove the residual solvent at nitrogen atmosphere in a glove box. Finally, the structure of TmPyPB(50 nm)/LiF(1 nm)/Al(150 nm) was thermally deposited in sequence in a vacuum chamber with a pressure less than  $4 \times 10^{-4}$  Pa through a shadow mask with an array of 14  $\text{mm}^2$  openings. The current density-voltage-luminance ( $I$ – $V$ – $L$ ) characteristics were measured using a Keithley source measurement unit (Keithley 2400) with a calibrated silicon photodiode. The EL spectra of the devices were measured using a SpectraScan PR650 spectrophotometer. All measurements were carried out at room temperature under ambient conditions.

### 2.3. Synthesis

#### 2.3.1. Synthesis of 1,8-bis(4-*tert*-butylphenyl)pyrene (**2a**)

Under the atmosphere of nitrogen, the mixture of 1,8-dibromopyrene (85%) and 1,6-dibromopyrene (15%) (1.80 g, 5 mmol) [27], 4-*tert*-butylphenylboronic acid (2.14 g, 12 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.12 g, 0.1 mmol) and 2 M potassium carbonate solution (12 mL) were dissolved in toluene (80 mL) and refluxed for 24 h. After the reaction finished, the mixture was poured into water and extracted with dichloromethane. The organic layer was dried over  $\text{MgSO}_4$  and the solvent was removed under vacuum. Then, the crude products were purified by silica gel column chromatography using hexane/dichloromethane mixture as eluent afforded a mixture of **2a** and **2b**. Finally, the mixture was recrystallized from dichloromethane/ethanol (1:2) solution and the pure compound **2a** was obtained as white needle-like crystals. Yield: 1.7 g, 73%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 8.0$  Hz, 2H), 8.21 (s, 2H), 8.13 (s, 2H), 8.03 (d,  $J = 7.6$  Hz, 2H), 7.59 (d,  $J = 16$  Hz, 8H), 1.48 (s, 18H).  $^{13}\text{C}$



**Scheme 1.** The strategy for new symmetrically pyrene-based photoelectric materials, where arylamine attachment is diphenylamino (**4a**), 4-(diphenylamino)phenyl (**4b**) and 4-(carbazol-9-yl)phenyl (**4c**).

Download English Version:

<https://daneshyari.com/en/article/175428>

Download Persian Version:

<https://daneshyari.com/article/175428>

[Daneshyari.com](https://daneshyari.com)