



A new series of short axially symmetrically and asymmetrically 1,3,6,8-tetrasubstituted pyrenes with two types of substituents: Syntheses, structures, photophysical properties and electroluminescence



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ABSTRACT

A new series of short axially symmetrically (**4a** and **4b**) and asymmetrically (**4c** and **4d**) 1,3,6,8-tetrasubstituted pyrene-based compounds with two phenyl moieties and two diphenylamine units on the 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 structures of **4a** and **4b** were determined by single-crystal X-ray diffraction analysis, indicating that the compounds are twisted by the peripheral substituents and the intermolecular π - π interactions have been efficiently interrupted. The four compounds exhibit high absolute fluorescence quantum yields (Φ_F) in dichloromethane (83.31–88.45%) and moderate Φ_{FS} in film states (20.78–38.68%). In addition, compounds **4a** and **4b** display relatively higher absolute Φ_{FS} than those of **4c** and **4d** in film states. All the compounds exhibit high thermal stability with decomposition temperatures above 358 °C and the values of **4c** and **4d** are higher than **4a** and **4b**. Compounds **4a** and **4b** can form morphologically stable amorphous thin films with T_g values of 146 °C and 149 °C, respectively. However, there are no obvious T_g observed in compounds **4c** and **4d**. Electroluminescent devices using **4a** and **4b** as doped emission layer show promising device performance with low turn-on voltage (3.0 V), maximum brightness around 15100 cd/m² and 16100 cd/m², maximum luminance efficiency of 12.4 cd/A and 13.6 cd/A and maximum external quantum efficiency of 5.34% and 5.63%, respectively.

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1. Introduction

Pyrene as one of the most known polyaromatic hydrocarbons (PAHs) has been paid everlasting attention in the development of organic fluorescent materials [1–5]. In recent years, numerous investigations have been carried out on the design and synthesis of pyrene-based compounds and their applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic devices (OPVs) because of their excellent fluorescence property, outstanding thermal stability, high charge carrier mobility and hole-injection ability [6–11]. To develop more excellent pyrene-based materials, the effective strategy is to tune the molecular structures and the photoelectric properties by

introducing different peripheral attachments into the suitable positions of pyrene core [10,12,13]. Indeed, a larger number of pyrene-based compounds with various peripheral groups and interesting photoelectric properties have been synthesized and exploited as efficient emitting and transporting materials for high performance photoelectric devices [10,14–17]. Furthermore, some pyrene-based materials have been exploited as emitters for conventional solution-processed organic electronic devices, since they have sufficient solubility and good film-forming abilities [18–20].

Among the many different modification methods on the pyrene core for novel pyrene-based photoelectric materials, the 1,3,6,8-tetrasubstituted pyrene-base compounds have the special advantages which facilitates not only the controlling on the intermolecular interactions but also the intramolecular electronic distribution [3,21–23]. For example, the incorporation of phenyl moieties, ethynyl groups and trimethylsilyl units at the 1,3,6,8-positions in pyrene can twist the structure and prevent excimer formation,

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resulting in dramatic improvement in the photoluminescence properties, especially in the fluorescence quantum yield [24–28]. However, to the best of our knowledge, most of the reported 1,3,6,8-tetrasubstituted pyrene compounds are modified using the same substituents. There are very few examples of symmetrically and asymmetrical 1,3,6,8-tetrasubstituted pyrenes with different peripheral segments on the pyrene ring due to the difficulty in synthesis and separation [16,23].

Based on the above considerations, we designed and synthesized a series of short axially symmetrically and asymmetrically 1,3,6,8-tetrasubstituted pyrenes with two phenyl moieties and two diphenylamine units on the pyrene core through the stepwise derivatization and functional transformation strategy using pyrene as the precursor (Scheme 1). The intermolecular interactions between the planar pyrene rings can be prevented by the peripheral phenyl segments and diphenylamine groups and the incorporation of arylamine units can improve the hole-injection and hole-transporting capability of the materials. Moreover, such architectures with two different substituents can more efficiently optimize the intramolecular electron distribution than those of 1,3,6,8-tetrasubstituted pyrenes with the same peripheral groups [16,29,30]. Herein, we report the design, synthesis, photoelectrical and electroluminescence properties of short axially symmetrically and asymmetrically 1,3,6,8-tetrasubstituted pyrenes with two types of substituents.

2. Experimental section

2.1. General

Dichloromethane was distilled from calcium hydride. All other chemicals were purchased from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were collected on a Bruker-400 MHz or Bruker-600 MHz spectrometer in CDCl_3 solution with TMS as an internal standard. Mass spectra were obtained on a Bruker Ultraflex extreme MALDI TOF/TOF mass spectrometer. Elemental analysis (C, H, N) of the dried solid samples were carried out using an Elementary Vario El analyzer. 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 (Φ_F) were determined by FM-4P-TCSPC Transient State Fluorescence Spectrometer using an integrating sphere for dilute dichloromethane 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 min^{-1} and cooled at 10 °C min^{-1} then heated again under the same heating conditions as used in the initial heating process, the values of T_g were determined from the second heating scan. Decomposition temperatures (T_d) were determined with thermogravimetric analysis (TGA) under a nitrogen atmosphere by using a DTG-60AH (Shimadzu). Samples were heated to 700 °C at a rate of 10 °C min^{-1} . Crystals data of compounds were selected on a Bruker APEX II CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K using the ω -scan technique. The structures were solved by direct methods with the SHELXS-97 computer program, and refined by full-matrix least-squares methods (SHELXL-97) on F^2 [31]. 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 09 W software package [32]. The electronic transitions were calculated using the time-dependent DFT (B3LYP) theory and the 6-31G (d, p) basis set.

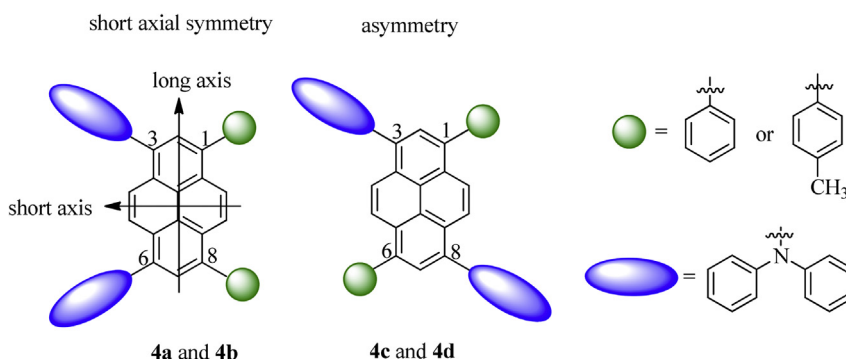
2.2. OLED fabrication and performance evaluation

ITO-coated glasses with a sheet resistance of 30 Ω per square were used as substrates. Before the devices were fabricated, the substrates were first cleaned with acetone, ethanol, and deionized water. Then, they were oven-dried at 120 °C and treated with UV-ozone under ambient conditions for 5 min. Finally, the cleaned glasses were transferred to a vacuum deposition system at approximately 4×10^{-4} Torr. Thermally evaporated organic layers were sequentially grown onto the ITO substrates at a rate of $1\text{--}2 \text{ \AA s}^{-1}$. The cathode was completed via the thermal deposition of Cs_2CO_3 at a rate of 0.1 \AA s^{-1} and then covered with Al metal deposited at a rate of 10 \AA s^{-1} . EL luminances and spectra were obtained using an AvaSpec-ULS2048L fiber spectrometer, and the current–voltage characteristics were determined with a computer-controlled Keithley 4200 SCS in ambient atmosphere. EQE was calculated from the current density, luminance, and EL spectrum, assuming a Lambertian distribution.

2.3. Synthesis

2.3.1. Synthesis of 1,8-diphenylpyrene (2a)

Under the atmosphere of nitrogen, the mixture of 1,8-



Scheme 1. The strategy for new 1,3,6,8-tetrasubstituted pyrene-based photoelectric materials (4a–4d).

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