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Review

Synthesis and properties of a new class of aggregation-induced enhanced emission compounds: Intense blue light emitting triphenylethylene derivatives

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ABSTRACT

A new series of fluorescent carbazole derivatives bearing linear alkyl chains with aggregation-enhanced emission properties have been synthesized. The compounds were fully characterized by elemental analysis, mass spectrometry and nuclear magnetic resonance spectroscopy. The compounds have high decomposition temperatures of 310–361 °C and exhibit intense blue fluorescence with maximum emission wavelengths at 445–473 nm. All the compounds emit weakly in solutions, but become strong emitters in the aggregated state and the photoluminescence intensity values increase up to 14 fold. An emitting device was fabricated using one of the compounds in the emitting layer which exhibits good electroluminescent performance with a blue emission color ($\lambda = 478$ nm), a turn-on voltage of 3.6 V and a maximum luminance of 1463 cd/m^2.

1. Introduction

Small molecule and polymer organic light-emitting diodes (OLEDs) have attracted considerable attention due to their great application potential in large area flat panel displays and solid state lighting [1]. Generally, most luminescent compounds exhibit strong luminescence in dilute solution, whereas, in high concentration solution or in the solid-state, their emissions are either often reduced or are relatively weak. The organic emissive materials in the devices are normally used as thin solid films in which aggregation is inherently accompanied with film formation [2,3]. Aggregation quenching seemed to be an intractable problem in the development of optoelectronic devices until aggregation-induced emission (AIE) and aggregation-induced enhanced emission (AIEE) [45] materials whose aggregates can emit more efficiently than their solutions were reported.

In order to improve the efficiency of OLEDs, great efforts have been devoted to develop high-performance AIE and AIEE materials. Solubility is important to the practical applications of organic luminescent materials for the purification of the product and fabrication of the electroluminescent device through spin-coating or ink-jet printing processes. However, the solubility of many highly conjugated organic luminescent materials is normally quite low [6]. To improve its solubility, introducing linear alkyl chains into a luminescent molecular structure may be an effective solution and may facilitate the deposition of high-quality films. On the other hand, the thermal stability of organic compounds is critical to the stability and lifetime of photoelectric devices [78] as well. Carbazole derivatives are a class of compounds that display strong blue light emissions, high *Tg* temperatures and AIEE effects [6], making them attractive candidates for the design of OLEDs.

In this paper, we report the synthesis of a new series of triphenylethylene carbazole derivatives containing different lengths of linear alkyl chains with strong blue light emission properties, high thermal stability and AIEE effect (Scheme 1). The photophysical, thermal, AIEE, electrochemical, and device properties were evaluated. It is expected that these molecules are potential materials for blue-light emitters in luminescent devices.

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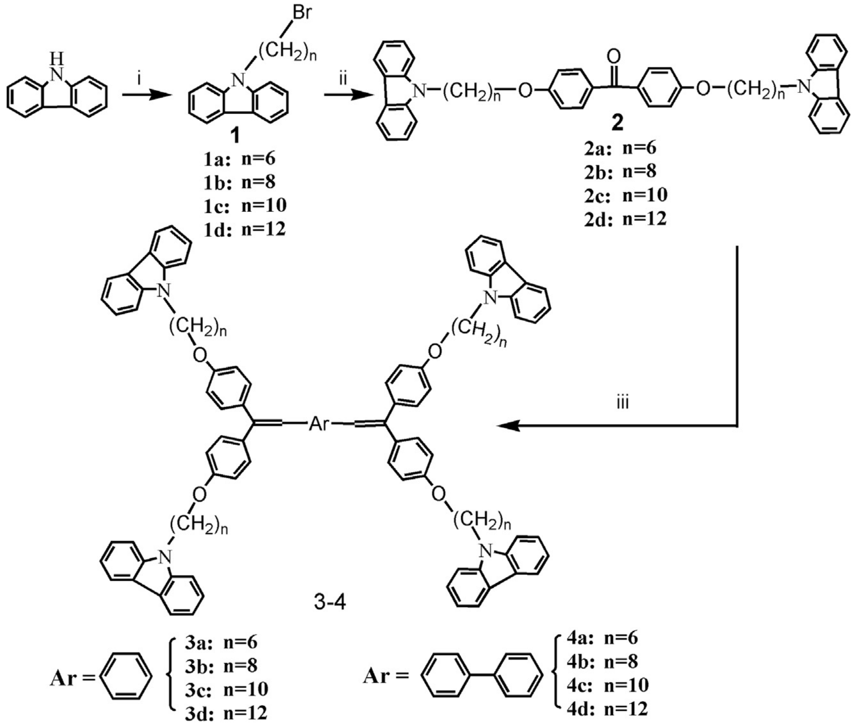

Scheme 1. Synthetic routes to the derivative. Reagents and conditions:(i) $C_nH_{2n}Br_2$, acetone, KOH, RT, 24 h; (ii) 4,4′-dihydroxybenzophenone, K_2CO_3, NaI, DMF, 60 °C, 12 h; (iii) diphosphonates, potassium *tert*-butoxide, THF, RT, 5 h.

2. Experimental section

2.1. Materials and methods

All starting reagents and chemicals were purchased from Alfa-Aesar and used as received. Tetrahydrofuran (THF) was redistilled with sodium benzophenone. Analytical grade N,N-dimethylformamide (DMF) was purified by distillation under an inert nitrogen atmosphere. Ultrapure water was used in the experiments. All other analytical-grade solvents were purchased from Guangzhou Damao Chemical Reagent Company and used without further purification.

NMR spectra were measured on a Varian Systems 400 MHz spectrometer. Mass spectra were measured on a Thermo MAT95XP-HRMS spectrometer. Elemental analyses were performed with an Elementar Vario EL elemental analyzer. Thermogravimetric analyses were performed with a NETZSCH spc-409 thermal analyzer under N_2 atmosphere at a heating rate of 10 °C/min. Fluorescence spectra were determined with a Hitachi FL-2500 spectrometer. UV–vis absorption spectra were recorded on a Shimdzu UV-1700 spectrophotometer. The fluorescence quantum yields(Φ_{FL}) of all the compounds in THF or THF/water mixture were evaluated using 9,10-diphenylanthracene as the reference [9]. Scanning electron microscopy images were obtained by a JEOL JSM-7600F field emission scanning electron microscope.

Cyclic voltammetry was carried out on a Shanghai Chenhua electrochemical workstations CHI-660C. The measurements were performed with a conventional three-electrode cell with ITO glass as the working electrode, Ag/Ag + nonaqueous electrode as the reference electrode, and platinum wire electrode as the auxiliary electrode, supported in 0.1 M $TBAAsF_6$ (TBA, tetrabutylammonium) in acetonitrile and CH_2Cl_2 (V/V = 1/1). All CV measurements were performed under an inert argon atmosphere at a scan rate of 100 mV s^{-1} using ferrocene (Fc) as the standard.

2.2. Device fabrication and testing

Indium–tin oxide(ITO)-coated glass with a sheet resistance of 20 Ω/sq was used as the substrate. The substrate was prepatterned to give an effective device size of 4 mm^2. Pretreatment of ITO includes routine chemical cleaning using detergent and alcohol in sequence. Poly(3,4-ethylenedioxythiophene)(PEDOT) was used as the hole-transporting layer. For spin-coated devices, PEDOT (Bayer) was coated from water dispersion on the ITO substrate, yielding a 100 nm thick layer after drying (ca. 105 °C; 5 min), and then coated with the active layer from toluene solutions containing 10 mg/mL compound 4a to give a film thickness of 80 nm. Finally, CsF (1.5 nm) and Al cathodes (100 nm) were thermally deposited onto the emitting-layers in a vacuum with a back pressure of 5×10^{-4} Pa. Electroluminescence (EL) spectrum was measured by a PR-650 spectroscan spectrometer. The brightness–current–voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley 2400 programmable electrometer. All measurements were carried out at room temperature under ambient conditions.

2.3. Synthesis

2.3.1. 9-(6-bromohexyl)-9H-carbazole (**1**a)

A solution of carbazole (3.00 g, 18 mmol) and corresponding 1,6-dibromohexane (28.1 g, 115 mmol) in acetone (35 mL) was stirred under a nitrogen atmosphere at room temperature for 30 min. Thereafter, KOH (4.3 g, 76.6 mmol) was added and the mixture was stirred for 24 h. After that, the mixture was poured into water and extracted three times with dichloromethane(3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with dichloromethane/n-hexane (1: 6,v/v) as eluent to give a white solid (3.68 g, 62% yield). Mp