



Easy accessible blue luminescent carbazole-based materials for organic light-emitting diodes



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ARTICLE INFO

Article history:

Received 6 July 2016

Received in revised form

26 September 2016

Accepted 29 September 2016

Available online 30 September 2016

Keywords:

Carbazoleo

Luminescenceo

Organic semiconductoro

Amorphous materialso

OLEDso

DFT calculationso

ABSTRACT

The thermal, optical, electrochemical and charge transport properties of a series of nine straightforward carbazole-based compounds have been analysed and interpreted according to their molecular structure by means of the X-ray analysis of single crystals. A non-doped OLED device with low turn-on voltage and maximum luminance up to 1.4×10^4 cd m⁻² was achieved. DFT calculations have been performed to explain the high efficiency of radiative exciton production.

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1. Introduction

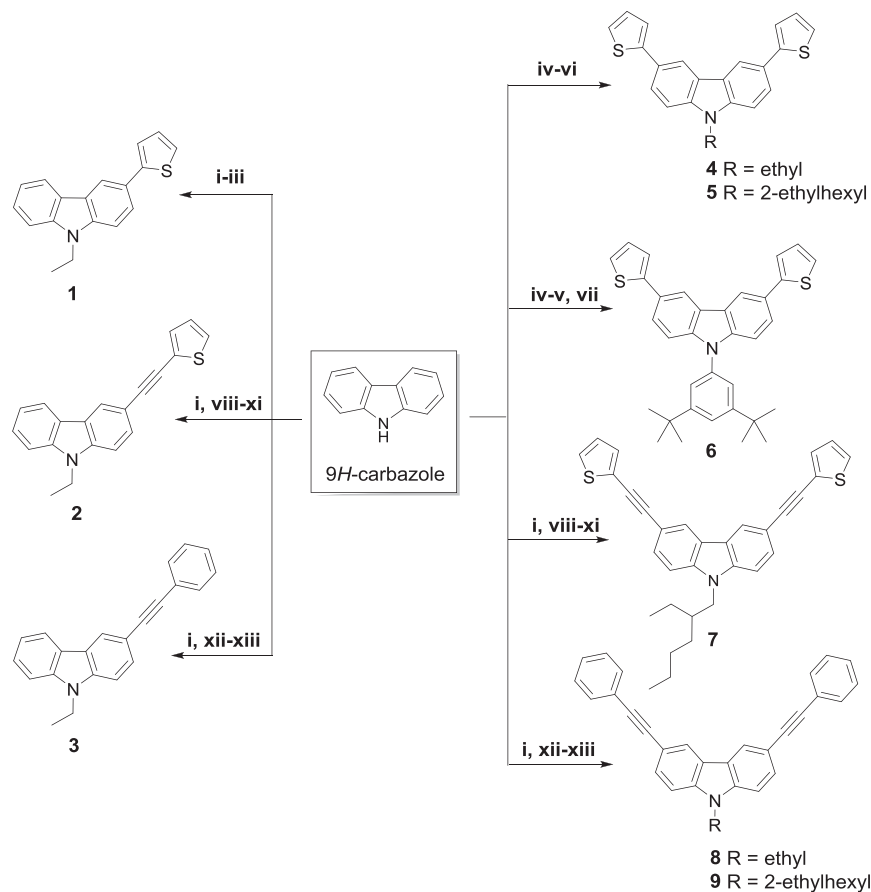
During the last decades organic light-emitting diodes (OLEDs) have evolved into commercial applications as flat-panel displays or artificial sources of solid-state lighting. Taking into account the inferior performance of blue OLEDs in front of the red and green ones and that efficient blue emitter materials are required in full-colour displays and white OLEDs (WOLEDs) [1], many research efforts are still currently put forward to the development of new luminescent dyes with blue emission [2]. Indeed, proper operation of OLED devices with blue-emitting materials is subjected to its intrinsic large band gaps that difficult the injection of charges into the emitting layer [3]. Therefore, the development of new blue emitters with thermal stability and capability to form amorphous thin films, together with high quantum yields in the solid state and colour purity is still required in order to give rise to OLED devices with high power efficiencies and longer operational lifetimes.

Carbazole derivatives have been used for a wide range of electronic and optoelectronic applications, for instance organic thin-film transistors (OTFTs) [4], organic solar cells [4d,5] and certainly OLEDs [6], due to their high thermal stability, emission efficiencies, easy chemical functionalization, film-forming capability and their potential hole-transporting mobility associated to the electron-donating ability of the carbazole unit [4a,7]. Therefore, among the many known luminescent materials with blue emission, carbazole derivatives are found to be promising as emitting layers in non-doped blue OLED devices [8].

This work is focused on simple structures and easy accessible carbazole derivatives, where different structural parameters were varied in order to study their influence on the thermal, optical and electrochemical properties. As a first factor, and with the aim of obtaining blue-emitting materials with high hole-transporting properties, it was considered to extend the π -conjugated carbazole system by introducing donor moieties, specifically the phenyl or thienyl units, at 3,6 positions of the carbazole core. In this way, mono- and di-substituted derivatives **1–9** were synthesized (Scheme 1). Besides, taking into account that π -conjugated linkers can significantly modulate the conjugation connectivity of the

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Scheme 1. Synthesis of compounds **1–9**. Reagents and conditions: (i) KI, KIO₃, acetic acid, reflux. (ii) 2-(Tributylstannyl)thiophene, Pd(PPh₃)₄, DMF, 100 °C. (iii) 1] NaH, DMF, RT. 2] Bromoethane, DMF, RT. (iv) NBS, SiO₂, CH₂Cl₂, RT. (v) 2-Thienylboronic acid, Pd(PPh₃)₄, K₂CO₃ 2M (aq), THF, reflux. (vi) 1] NaH, DMF, RT. 2] Bromoethane/2-Ethylhexyl bromide, DMF, RT. (vii) 1-Bromo-3,5-di-*tert*-butylbenzene, K₂CO₃, Cu, DMF, reflux. (viii) Ethynyltrimethylsilane, Pd(PPh₃)₂Cl₂, CuI, Et₃N, THF, RT. (ix) K₂CO₃, MeOH, RT. (x) 2-Iodothiophene, Pd(PPh₃)₂Cl₂, CuI, Et₃N, THF, RT. (xi) 1] NaH, DMF, RT. 2] Bromoethane/2-Ethylhexyl bromide, DMF, RT. (xii) Phenylacetylene, Pd(PPh₃)₂Cl₂, CuI, Et₃N, THF, RT. (xiii) 1] NaH, DMF, RT. 2] Bromoethane/2-Ethylhexyl bromide, DMF, RT.

molecules and the photophysical properties [9], the effect of the insertion of a triple bond as a π -conjugated linker between the carbazole and the donor units was also analysed. As a last structural variation, the nature of the N-substitution of the carbazole core was modified from the alkyl chains, ethyl and 2-ethylhexyl, to the bulky 3,5-di-*tert*-butylphenyl fragment. To gain insight into the structure-properties relationship of this series of carbazole derivatives and the mechanism through which emission occurs, solid state structures were analysed by X-ray diffraction (XRD) and density functional theory (DFT) calculations were performed. From the study of the structure-properties relationship, compound **8** was selected for its evaluation as the emitting layer in non-doped OLED devices.

2. Experimental

2.1. Materials

All reagents for synthesis were obtained from commercial sources and were used as received. Solvents were dried and degassed by standard methods. Tetrahydrofuran was distilled from sodium/benzophenone in a nitrogen atmosphere. The synthesis of 3,6-dibromo-9H-carbazole [10], 3-iodo-9H-carbazole [11] and 3,6-diiodo-9H-carbazole [11] is described in the literature. 3-(2-Thienyl)-9H-carbazole [12] and 3,6-di-2-thienyl-9H-carbazole [13] were obtained from 3-iodo-9H-carbazole and 3,6-dibromo-9H-carbazole, respectively, under reported methods. 3-Ethynyl-9H-

carbazole and 3,6-diethynyl-9H-carbazole were synthesized from 3-iodo-9H-carbazole and 3,6-diiodo-9H-carbazole according to reported procedures [14,15]. 3-(2-Phenylethynyl)-9H-carbazole and 3,6-bis(2-phenylethynyl)-9H-carbazole were prepared from 3-iodo-9H-carbazole and 3,6-diiodo-9H-carbazole, respectively, according to reported methods [14,16].

2.2. Synthesis and characterization

2.2.1. General synthetic procedure for the alkylation of 9H-carbazole derivatives

NaH (60% dispersion in mineral oil) (1.2–1.5 eq.) was added to a solution of the corresponding NH-carbazole (1 eq.) precursor in anhydrous DMF under nitrogen atmosphere. The solution was stirred at room temperature for 45 min. Then, the corresponding alkyl bromide (1.2–1.5 eq.) was added and the mixture was stirred at room temperature overnight and then treated with water. The aqueous layer was extracted with dichloromethane and the organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude was purified by flash column chromatography.

2.2.2. Synthesis of 9-ethyl-3-(2-thienyl)-9H-carbazole (**1**)

Prepared according to the general procedure for the alkylation reaction using as starting materials 3-(2-thienyl)-9H-carbazole (249 mg, 1.00 mmol), NaH (48 mg, 1.21 mmol, 60% dispersion in

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