



# Carbazolyl-substituted quinazolinones as high-triplet-energy materials for phosphorescent organic light emitting diodes



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## ABSTRACT

A series of carbazolyl-substituted quinazolinones were designed and synthesized by the Pd-catalyzed Buchwald-Hartwig, Suzuki and Heck cross-coupling reactions. Their optical, photophysical, thermal, electrochemical, and electroluminescent properties were investigated. The characterization of the synthesized compounds was carried out using experimental and theoretical methods. The determined geometries of the compounds lead to the HOMO distribution on the quinazolinone moiety and the different donor substituents. The synthesized compounds form glasses with the glass transition temperatures ranging from 97 to 159 °C. Their solutions in tetrahydrofuran absorb electromagnetic radiation in the range of 210–420 nm and emit in the range of 350–600 nm. The Stokes shifts recorded for the dilute solutions of compounds ranged from 48 to 134 nm, while those observed for the solid films were similarly in the range of 46–113 nm. The highest fluorescence quantum yield of 44.3% was recorded for the solution of 3-(9-ethyl-9H-carbazol-3-yl)-5-((E)-2-(9-ethyl-9H-carbazol-3-yl)ethenyl)-2-methylquinazolin-4(3H)-one. The triplet energy levels established for the dilute solutions of the compounds from their phosphorescence spectra at 77 K were found to be in the range of 2.55–2.99 eV. The ionization potentials of the synthesized compounds established by photoelectron emission technique in air ranged from 5.35 to 5.66 eV. The electrochemical properties of the derivatives were studied by cyclic voltammetry. All the studied compounds showed irreversible oxidation and no reduction waves. Their repeated cyclic voltammetry scans displayed increasing changes in the cyclic voltammetry traces, proving that a series of electro-polymerization reactions of the radical cations occurred. Time-of-flight hole drift mobility of the solid layer of 5-(bis(4-*tert*-butyldiphenyl)amino)-3-(9-ethyl-9H-carbazol-3-yl)-2-methylquinazolin-4(3H)-one reached  $1.1 \times 10^{-3} \text{ cm}^2/\text{Vs}$  at an electric field of  $8.1 \times 10^5 \text{ V/cm}$ . This compound was tested as a host in the green and blue phosphorescent organic light emitting diodes achieving maximum external quantum efficiencies of ca. 7.1 and 6.9%, respectively.

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## 1. Introduction

Organic materials possessing extended  $\pi$ -conjugation received great attention in recent years owing to their useful photophysical and charge transport properties, which make them potential materials for the application in electronic and optoelectronic devices [1,2].

Much effort was devoted to establish structure-property relationships in order to develop new materials with desired

properties. Due to the electron-donating capabilities associated with the nitrogen atom in the carbazole ring, derivatives of carbazole represent a very popular family of functional organic compounds because of their interesting optical properties, low redox potentials, high chemical and thermal stability, good charge-transporting properties [3,4]. Nitrogen atom of carbazole moiety can be functionalized by alkylation or arylation reactions to enhance the solubility and to improve other properties of the resulting derivatives [5]. Many carbazole-containing molecules are known to exhibit relatively intense luminescence and high glass transition temperatures [6,7]. For these reasons they have been extensively investigated for the applications in optoelectronic devices such as organic light-emitting diodes (OLEDs) and dye-

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sensitized solar cells [8,9]. Carbazole can also be easily functionalized by electrophilic aromatic substitution at its C-3, and C-6 positions with high electron density, and hence a large number of 3,6-functionalized carbazole derivatives were reported [10,11].

Quinazolinone derivatives were actively studied as they represent an important class of compounds due to their wide range of intrinsic biological activities [12]. Use of quinazolinone derivatives as semiconductors may potentially furnish capability of organic optoelectronic devices. To our knowledge, no systematic study on structurally well-defined carbazole-quinazolinone systems focusing on the effect of the connectivity between the carbazole and quinazolinone moieties on their electronic, optical, photoelectrical, electrochemical, and electroluminescent properties was reported so far. In this context, we became interested in 9-ethylcarbazolyl-substituted quinazolinone derivatives, in which the number of different electron-donating groups (3,6-di-*tert*-butylcarbazole, 4,4'-dimethoxydiphenylamine, 4,4'-di-*tert*-butyl-diphenylamine, 9-ethyl-3-vinyl-9*H*-carbazole, 2-(*N*-methylcarbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane) are linked at C-5 position of quinazolinone moiety.

Here, we report on the synthesis of differently-substituted quinazolinones and on their thermal, photophysical, photoelectrical, redox properties, and demonstrate the applicability of these materials as hosts for phosphorescence organic light emitting diodes. Joint experimental and theoretical approaches are employed in order to characterize the synthesized derivatives, and to better understand the structure-property relationships.

## 2. Experimental

### 2.1. Materials and instrumentation

2-Acetamido-5-bromobenzoic acid, 4,4'-dimethoxydiphenylamine, 4,4'-di-*tert*-butyl-diphenylamine, 3-amino-9ethylcarbazole, 9-ethyl-3-carbazolecarboxaldehyde, tri-*tert*-butylphosphine solution (1.0 M in toluene), tri(*o*-tolyl)phosphine (P(*o*-tolyl)<sub>3</sub>), palladium(II) acetate (Pd(OAc)<sub>2</sub>), bis(triphenylphosphine)palladium(II) (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>), triethylamine, phosphoryl chloride (POCl<sub>3</sub>), potassium *tert*-butoxide, methyltriphenylphosphonium bromide (CH<sub>3</sub>PPh<sub>3</sub>) were purchased from Aldrich, TCI Europe, Acros and used without further purification. Solvents were dried and purified by distillation.

3,6-Di-*tert*-butyl-9*H*-carbazole (**3a**) [13] (m.p. 221–222 °C, lit. [14] m.p. 228 °C), 2-(*N*-methylcarbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (**3b**) [15] (m.p. 143–144 °C, lit. [15] m.p. 150.6–151.8 °C), 9-ethyl-3-vinyl-9*H*-carbazole (**3c**) [16] (m.p. 62–63 °C, lit. [17] m.p. 66–67 °C) were prepared according to the published procedures.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Varrian Unity Inova (300 MHz (<sup>1</sup>H), 75.4 MHz (<sup>13</sup>C)) spectrometer at room temperature. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyzer. Differential scanning calorimetry (DSC) measurements were carried out using a Q100 TA DSC series thermal analyzer at a heating rate of 10 °C/min under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851<sup>c</sup> under nitrogen. Melting points were recorded on Electrothermal MEL-TEMP melting point apparatus. UV absorption spectra were recorded on Perkin Elmer Lambda 35 spectrometer. Fluorescence spectra were recorded with a Perkin Elmer LS 55 and Edinburgh Instruments FLS980 spectrometers. Phosphorescence spectra were recorded on Edinburgh Instruments FLS980 spectrometer at

the temperature of liquid nitrogen (nominally 77 K). Fluorescence quantum yields ( $\Phi_F$ ) of the solutions and solid films were carried out by absolute method with FLS980 fluorescence spectrometer and using integrating sphere of 120 mm inside diameter of the spherical cavity. All the measurements were carried out at the room temperature. Solid-state ionization potentials (IP<sub>PE</sub>) were established by electron photoemission in air method as reported earlier [18,19]. For the measurements the layers on ITO glass were prepared by drop casting from the solutions of the compounds in tetrahydrofuran (THF). The samples were illuminated with the monochromatic light obtained using the deep UV deuterium light source ASBN-D130-CM and CM110 1/8 m monochromator. The negative voltage of 500 V was supplied to the sample substrate. The counter-electrode was placed at the distance of 3 mm from the sample surface. The counter-electrode was connected to the input of the 6517B Keithley electrometer for the photocurrent measurement. An energy scan of the incident photons was performed while increasing the photon energy  $h\nu$ . In this scan direction, no electrons were emitted until  $h\nu$  exceeded the ionization potential of the layer. The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon, the reference electrode and the counter electrode were Ag/Ag<sup>+</sup> 0.01 M and Pt wire, respectively. Argon-purged dichloromethane (DCM) with tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NBF<sub>6</sub>) 0.1 M was used as electrolyte. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox system [20]. Half-wave redox potential for Fc/Fc<sup>+</sup> was established to be 0.285 V vs. Ag. The charge mobilities of the studied materials were estimated by the time-of-flight (TOF) technique [21]. The layers for the TOF measurements were prepared by a vacuum vapor deposition onto precleaned glass substrates with indium-tin oxide (ITO) electrodes at vacuum below  $3 \times 10^{-6}$  mBar. The layer of aluminum with the thickness of a 60 nm was deposited on the organic film as the upper electrode. The thickness of the organic layers was between 1.3 and 5  $\mu$ m. The measurements were carried out at room temperature. For generation of charge carriers a Nd:YAG laser (EKSPLA NL300) with the wavelength of 355 nm and 3–6 ns pulse width was used as a light source. Electric fields were applied by a 6517B Keithley electrometer. The photocurrent was measured with a digital stragescope Tektronix TDS 3032C through a resistance. The transit times  $t_{tr}$  were used to calculate the charge carrier mobility  $\mu$  by the equation  $\mu = d^2/Vt_{tr}$ , where  $d$  is the thickness of the studied films and  $V$  is the applied voltage to the electrodes of the TOF structures. Phosphorescent OLEDs (PhOLEDs) were fabricated by thermal vacuum deposition under the vacuum higher than  $3 \times 10^{-6}$  mBar. The host:guest emission layers from two different sources were deposited by co-deposition of host (m/m 90%) with deposition rate of ca. 1 Å/s and dopant (m/m 10%) with deposition rate of ca. 0.1 Å/s. A Keithley source meter 2400-C, a 6517B Keithley electrometer, a calibrated silicon photodiode plashed in front of the PhOLEDs, and an Avantes AvaSpec-2048XL spectrometer were utilized for recording of the current density-voltage and current density-luminance characteristics and electroluminescence (EL) spectra of the devices. The current, power and external quantum efficiencies were estimated utilizing the current density, luminance, and EL spectra as reported earlier [22]. Density function theory (DFT) and time dependent density function theory (TDDFT) were performed using Gaussian 09 software employing B3LYP functional and 6-31G(d,p) basis set [23]. Up to 40 excited states were calculated and theoretical absorption spectra were obtained by considering a band half-width at half-maximum of 0.3 eV.

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