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Graphical abstract



Carbazolyl-substituted quinazolinones as high-triplet-energy materials for

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Dalius Gudeika¹, Dmytro Volyniuk¹, Viktorija Mimaite¹, Roman Lytvyn², Rita Butkute¹, Oleksandr Bezvikonnyi¹, Gintaras Buika¹, Juozas V. Grazulevicius^{1*}

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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 guinazolinone 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-9*H*-carbazol-3-yl)-2-methylquinazolin-4(3H)-one reached 1.1×10^{-3} cm²/Vs at an electric field of 8.1×10^{5} 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.

Keywords: quinazolinone, Buchwald-Hartwig, Suzuki, Heck reactions, organic light emitting diode, electro-polymerization reaction.

1. INTRODUCTION

Organic materials possessing extended π -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-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 aproaches 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*-butyldiphenylamine, 3-amino-9*H*-ethyl-carbazole, 9-ethyl-9*H*-carbazole-3-carbaldehyde, tri-*tert*butylphosphine solution (1.0 M in toluene), tri(*o*-tolyl)phosphine (P(*o*-tolyl)₃), palladium(II) acetate (Pd(OAc)₂), bis(triphenylphosphine)palladium(II) (Pd(PPh₃)₂Cl₂), triethylamine, phosphoryl chloride (POCl₃), potassium *tert*-butoxide, methyltriphenylphosphonium bromide (CH₃PPh₃) 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.

¹H and ¹³C NMR spectra were recordered using Varrian Unity Inova (300 MHz (¹H), 75.4 MHz (¹³C)) 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 Analyser. 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^e 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 at the temperature of liquid nitrogen (nominally 77 K).

Fluorescence quantum yields ($\Phi_{\rm F}$) of the solutions and solid films were carried out by absolute method with FLS980 fluorescence spectrometer and using integrating sphere of 120 mm inside diametre of the spherical cavity. All the measurements were carried out at the room temperature. Solid-state ionization potentials (IP_{PE}) 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 counterelectrode 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 hv. In this scan direction, no electrons were emitted until hv 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⁺ 0.01 M and Pt wire, respectively. Argon-purged dichloromethane (DCM) with tetrabutylammonium hexafluorophosphate (Bu₄NBF₆) 0.1 M was used as electrolyte. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc⁺/Fc) redox system [20]. Half-wave redox potential for Fc/Fc⁺ 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 $3 \cdot 10^{-6}$ 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 μ 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 μ 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 3×10^{-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 plased 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.

2.2. Synthesis

5-Bromo-3-(9-ethyl-9*H***-carbazol-3-yl)-2-methylquinazolin-4(3H)-one (2a).** *N*-Acetyl-5-bromo anthranilic acid (**1a**) (5 g, 19.38 mmol) was added to a solution of 3-amino-9-ethyl-carbazole (**1b**) (4.05 g, 19.31 mmol) in dry toluene (60 ml). POCl₃ (12 ml) was added dropwise during 40 min with stirring, and then the reaction mixture was refluxed for 8 hrs. After cooling to the room temperature, the reaction mixture was diluted with ice-water, treated with 15% K₂CO₃ solution and extracted with chloroform. The organic phase was dried over Na₂SO₄, concentrated and the crude product was purified by column chromatography using hexane/toluene (1:3) as eluent followed by recrystallization from the solvent mixture of eluent to obtain **2a** (yield: 5.69 g, 68%), m.p. 270-272 °C. ¹H NMR

spectrum (300 MHz, DMSO, δ , ppm): 8.25 (d, 1H, J = 2.0 Hz, Ar), 8.22 (d, 1H, J = 2.4 Hz, Ar), 8.16 (d, 1H, J = 7.8 Hz, Ar), 8.03 (dd, 2H, $J_I = 7.8$ Hz, $J_2 = 2.4$ Hz, Ar), 7.80 (d, 1H, J = 8.7 Hz, Ar), 7.68 (d, 1H, J = 8.7 Hz, Ar), 7.57-7.48 (m, 2H, Ar), 7.26 (t, 1H, J = 7.5 Hz, Ar), 4.54 (q, 2H, $J_I = 7.2$ Hz, $J_2 = 7.2$ Hz, -CH₂), 2.20 (s, 3H, -CH₃), 1.39 (t, 3H, J = 7.2 Hz, -CH₃). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ , ppm): 162.21, 148.06, 145.35, 135.63, 132.98, 132.15, 131.72, 128.66, 125.27, 123.83, 122.58, 120.25, 118.92, 117.11, 114.25, 112.08, 111.53, 108.26, 102.36, 100.73, 48.22, 22.82, 15.02. IR (KBr), υ , cm⁻¹: 3438 (C-H_{ar}), 2962, 2931 (C-H_{aliph}), 1682 (C=O_{quinazolinone}), 1607, 1519, 1484 (C=C_{ar}), 1271, 1188 (C-N), 1011, 989 (CH_{ar}). MS (APCI⁺, 20 V), m/z: 433 ([M+H]⁺).

5-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-3-(9-ethyl-9H-carbazol-3-yl)-2-methylquinazolin-

4(3H)-one (1). The mixture of 2a (0.5 g, 1.16 mmol), 3,6-di-tert-butyl-9H-carbazole (3a) (0.39 g, 1.39 mmol), Pd(OAc)₂ (0.012 g, 0.058 mmol), tri-*tert*-butylphosphine solution (1.0 M in toluene) (0.008 g, 0.038 mmol), potassium tert-butoxide (0.32 g, 2.89 mmol) and 25 ml of dry toluene was heated at 120 °C for 24 h under nitrogen. After cooling, the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine. After being dried over MgSO₄ and filtered, the solvent was removed and the residue was purified by column chromatography using hexane/toluene (1:3) as eluent to obtain amorphous compound **1** (yield: 0.46 g, 64 %). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.54 (d, 1H, *J* = 2.3 Hz, Ar), 8.17 (d, 2H, *J* = 1.4 Hz, Ar), 8.10 (d, 1H, *J* = 7.7 Hz, Ar), 8.03 (dd, 2H, J₁ = 7.7 Hz, J₂ = 2.4 Hz, Ar), 7.99 (d, 1H, J = 2.4 Hz, Ar), 7.94 (d, 1H, J = 8.6 Hz, Ar), 7.61 (d, 1H, J = 8.6 Hz, Ar), 7.56 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.1$ Hz, Ar), 7.49 (dd, 2H, $J_1 = 1.1$ Hz, Ar), 7.49 (dd, 2H, $J_2 = 1.1$ Hz, Ar), 7.49 (dd, 2H, J_2 = 1.1 7.7 Hz, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_1 = 7.7$ Hz, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_1 = 8.6$ Hz, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_1 = 8.6$ Hz, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_1 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 1H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.39 (dd, 2H, $J_2 = 1.4$ Hz, Ar), 7.45 (dd, 2H, J_2 = 1.4 Hz, Ar), 7.45 (dd, 2.1 Hz, Ar), 7.32-7.29 (m, 1H, Ar), 4.52-4.41 (m, 2H, -CH₂), 2.39 (s, 3H, -CH₃), 1.52 (t, J = 7.2 Hz, 3H, -CH₃), 1.45 (s, 18H, $2 \times C(CH_3)_3$). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ , ppm): 162.6, 155.7, 146.1, 143.3, 140.7, 139.8, 139.0, 136.6, 132.9, 128.6, 126.5, 124.9, 124.3, 124.2, 123.9, 123.8, 122.3, 122.2, 120.8, 119.9, 119.4, 116.3, 109.7, 109.1, 108.6, 34.7, 32.0, 26.9, 24.7, 13.9. IR (KBr), υ, cm⁻¹: 3031 (C-H_{ar}), 2925, 2832 (C-H_{aliph}), 1670 (C=O_{quinazolinone}), 1603, 1502, 1478 (C=C_{ar}), 1249, 1188 (C-

N), 1022, 819, 738 (CH_{ar}). Anal. Calc. for C₄₃H₄₂N₄O: C, 81.87; H, 6.71; N, 8.88; O, 2.54%. Found: C, 81.90; H 6.65; N, 8.93%. MS (APCI⁺, 20 V), m/z: 631 ([M+H]⁺).

5-(Bis(4-tert-butyldiphenyl)amino)-3-(9-ethyl-9H-carbazol-3-yl)-2-methylquinazolin-4(3H)one (2) was synthesized by the similar procedure as compound 1. The mixture of 2a (0.5 g, 1.16 mmol), 4,4'-di-tert-butyl-diphenylamine (0.39 g, 1.39 mmol), Pd(OAc)₂ (0.012 g, 0.058 mmol), tritert-butylphosphine solution (1.0 M in toluene) (0.008 g, 0.038 mmol), potassium tert-butoxide (0.32 g, 2.89 mmol) and 25 ml of dry toluene was used for the synthesis. The product was purified by column chromatography using hexane/toluene (1/2) as eluent followed by recrystallization from the eluent mixture of solvents to obtain white crystals of 2 (yield: 0.49 g, 67%), m.p. 292-293 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.06 (d, 1H, J = 7.8 Hz, Ar), 7.97 (d, 1H, J = 1.7 Hz, Ar), 7.89 (d, 1H, J = 2.4 Hz, Ar), 7.57-7.46 (m, 7H, Ar), 7.28-7.31 (m, 4H, Ar), 7.08 (d, 4H, J = 8.5 Hz, Ar), 4.52-4.37 (m, 2H, -CH₂), 2.28 (s, 3H, -CH₃), 1.50 (d, 3H, J = 7.2 Hz, -CH₃), 1.32 (s, 18H, -CH₃). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ, ppm): 163.3, 152.9, 146.9, 146.39 (s), 144.5, 142.3, 140.5, 139.6, 129.6, 129.1, 127.5, 126.3, 124.9, 124.3, 123.7, 122.4, 121.7, 120.7, 119.9, 119.3, 117.8, 109.4, 108.8, 53.4, 37.8, 34.3, 31.4, 24.4, 13.9. IR (KBr), v, cm⁻¹: 2996 (C-H_{ar}), 2916, 2816 (C-H_{aliph}), 1665 (C=O_{guinazolinone}), 1589, 1489, 1476 (C=C_{ar}), 1242, 1192 (C-N), 1018, 813, 731 (CH_{ar}). Anal. Calc. for C₄₃H₄₄N₄O: C, 81.61; H, 7.01; N, 8.85; O, 2.53%. Found: C, 81.28; H 7.33; N, 8.87%. MS (APCI⁺, 20 V), m/z: 634 ($[M+H]^+$).

5-(Bis(4-methoxyphenyl)amino)-3-(9-ethyl-9*H***-carbazol-3-yl)-2-methylquinazolin-4(3H)-one (3) was synthesized by the similar procedure as compound 1. The mixture of 2a** (0.5 g, 1.16 mmol), 4,4'-dimethoxydiphenylamine (0.32 g, 1.39 mmol), Pd(OAc)₂ (0.012 g, 0.058 mmol), tri-*tert*-butylphosphine solution (1.0 M in toluene) (0.008 g, 0.038 mmol), potassium *tert*-butoxide (0.32 g, 2.89 mmol) in 25 ml of dry toluene was used for the synthesis. The product was purified by column chromatography using hexane/toluene (1/2) as eluent followed by recrystallization from the mixture of solvents of the eluent to obtain white crystals of **3** (yield: 0.41 g, 61%), m.p. 238-239 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.06 (d, 1H, *J* = 7.8 Hz, Ar), 7.96 (d, 1H, *J* = 1.8 Hz, Ar), 7.74 (d, 1H, *J* =

2.7 Hz, Ar), 7.53-7.49 (m, 3H, Ar), 7.48 (d, 1H, J = 8.1 Hz, Ar), 7.42 (dd, 1H, $J_1 = 8.9$ Hz, $J_2 = 2.7$ Hz, Ar), 7.11-7.07 (m, 5H, Ar), 6.86-7.79 (m, 5H, Ar), 4.51-4.37 (m, 2H, -CH₂), 3.81 (s, 6H, -OCH₃), 2.27 (s, 3H, -CH₃), 1.51 (t, 3H, J = 7.2 Hz, -CH₃). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ , ppm): 163.3, 156.2, 152.8, 147.6, 141.6, 140.3, 139.7, 129.4, 129.3, 127.9, 127.6, 126.7, 126.4, 125.2, 123.9, 122.6, 121.8, 120.7, 119.9, 119.5, 115.5, 114.9, 109.4, 108.9, 68.0, 55.5, 25.6, 13.9. IR (KBr), ν , cm⁻¹: 3085 (C-H_{ar}), 2931, 2833 (C-H_{aliph}), 1676 (C=O_{quinazolinone}), 1602, 1506, 1483 (C=C_{ar}), 1241, 1197 (C-N), 1032, 828, 747 (CH_{ar}). Anal. Calc. for C₃₇H₃₂N₄O₃: C, 76.53; H, 5.55; N, 9.65; O, 8.27%. Found: C, 76.48; H 5.53; N, 9.71%. MS (APCI⁺, 20 V), m/z: 581 ([M+H]⁺).

3-(9-Ethyl-9H-carbazol-3-yl)-5-((E)-2-(9-ethyl-9H-carbazol-3-yl)ethenyl)-2-

methylquinazolin-4(3H)-one (4). The reaction mixture consisting of 2a (0.5 g, 1.16 mmol), 9-ethyl-3-vinyl-9*H*-carbazole (3c) (0.31 g, 1.39 mmol), Pd(OAc)₂ (0.017 g, 0.077 mmol), P(*o*-tolyl)₃ (0.018 g, 0.057 mmol), DMF (10 mL), and triethylamine (3 mL) was placed into the flask which was preliminarily degassed and purged with nitrogen. The mixture was heated at 90 °C for 24 h under N₂. Then, it was filtered, and the filtrate was poured into distilled water and extracted with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate and concentrated by vacuum evaporation. The crude product was purified by column chromatography using hexane/toluene (1/1) as eluent followed by recrystallization from the eluent mixture of solvents to obtain white crystals of **4** (yield: 0.31 g, 47%), m.p. 267-268 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.43 (d, 1H, J = 2.0 Hz, Ar), 8.30 (d, 1H, J = 1.4 Hz, Ar), 8.17 (d, 1H, J = 7.7 Hz, Ar), 8.12-8.02 (m, 3H, Ar), 7.74 (dd, 2H, $J_1 = 8.5$ Hz, $J_2 = 2.4$ Hz, Ar), 7.63-7.58 (m, 1H, Ar), 7.57-7.53 (m, 2H, Ar), 7.52-7.47 (m, 3H, Ar), 7.47-7.42 (m, 3H, Ar), 7.37 (dd, 1H, $J_1 = 8.6$ Hz, $J_2 = 2.1$ Hz, Ar), 7.31-7.25 (m, 1H, Ar), 4.50-4.37 (m, 4H, -CH₂), 2.34 (s, 3H, -CH₃), 1.55 (s, 3H, -CH₃), 1.42 (s, 3H, -CH₃). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ , ppm): 163.6, 154.8, 147.0, 140.5, 140.5, 139.9, 137.1, 131.9, 130.9, 128.9, 128.1, 127.1, 126.5, 126.5, 125.9, 124.9, 124.8, 122.9, 120.8, 120.5, 119.9, 119.4, 119.0, 109.6, 108.8, 37.7, 24.7, 13.9. IR (KBr), v, cm⁻¹: 3012 (C-H_{ar}), 2922, 2815 (C-H_{aliph}), 1667 (C=O_{auinazolinone}), 1603, 1511, 1481 (C=C_{ar}), 1243, 1172 (C-N), 955 (*trans*, -CH=CH), 818, 736 (CH_{ar}).

Anal. Calc. for C₃₉H₃₂N₄O: C, 81.79; H, 5.63; N, 9.78; O, 2.79%. Found: C, 81.71; H 5.62; N, 9.82%. MS (APCI⁺, 20 V), m/z: 573 ([M+H]⁺).

3-(9-Ethyl-9H-carbazol-3-yl)-2-methyl-5-(9-methyl-9H-carbazol-3-yl)quinazolin-4(3H)-one (5). The mixture of 2a (0.5 g, 1.16 mmol), 2-(N-methylcarbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3b) (0.4 g, 1.37 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.046 mmol), and Na₂CO₃ (1.6 g, 11.57 mmol) in 20 mL of THF/water (19/1 v/v) was degassed with nitrogen for 3-5 min. Then the reaction mixture was stirred at reflux under nitrogen for 24 h. After recooling, water (50 ml) was added and the mixture was extracted with CH₂Cl₂ (3×50 ml). The combined organic phase was washed with water (50 ml) and brine solution (50 ml), dried over anhydrous Na₂SO₄, filtered and the solvent was removed to dryness. Purification by column chromatography over silica gel eluting with the mixture of chloroform and hexane (3:1) followed by recrystallization from the mixture of solvents of the eluent enabled to obtain white crystals of 5 (0.32 g, 51%). M.p. 257-258 °C; ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.64 (s, 1H, Ar), 8.47 (s, 1H, Ar), 8.35-8.30 (m, 2H, Ar), 8.18 (d, 1H, J = 7.8 Hz, Ar), 7.91 (d, 1H, J = 8.6 Hz, Ar), 7.82 (dd, 2H, $J_1 = 8.6$ Hz, $J_2 = 3.8$ Hz, Ar), 7.72-7.68 (m, 2H, Ar), 7.63 (d, 1H, J = 8.6 Hz, Ar), 7.52-7.47 (m, 3H, Ar), 7.25-7.18 (m, 3H, Ar), 4.59-4.48 (m, 2H, -CH₂), 3.93 (s, 3H, -NCH₃), 2.24 (s, 3H, -CH₃), 1.40 (t, 3H, J = 7.1 Hz, -CH₃). ¹³C NMR spectrum (75.4 MHz, CDCl₃, δ, ppm): 158.2, 148.6, 146.8, 144.5, 135.8, 135.3, 133.6, 133.3, 131.6, 131.2, 131.1, 130.7, 126.4, 124.8, 123.6, 123.2, 122.1, 121.7, 121.2, 121.0, 120.6, 119.7, 119.5, 118.8, 114.4, 113.6, 112.3, 111.4, 111.1, 110.9, 108.4, 107.6, 49.3, 43.6, 22.1, 14.3. IR (KBr), v, cm⁻¹: 3035 (C-H_{ar}), 2929, 2834 (C-Haliph), 1672 (C=Oquinazolinone), 1605, 1509, 1481 (C=Car), 1253, 1182 (C-N), 1025, 821, 742 (CH_{ar}). Anal. Calc. for C₃₆H₂₈N₄O: C, 81.18; H, 5.30; N, 10.52; O, 3.00%. Found: C, 81.14; H 5.32; N, 10.57%. MS (APCI⁺, 20 V), m/z: 533 ([M+H]⁺).

3. RESULTS AND DISCUSSION

Scheme 1 shows synthetic routes to carbazolyl-substituted quinazalinones having different donor substituents at C-5 position of quinazolinone moiety. Commercially available 2-acetamido-5-bromobenzoic acid (**1a**) was condensed with 3-amino-9-ethyl-carbazole (**1b**) in refluxing POCl₃/toluene to obtain bromo quinazolinone **2a**. Compounds **1**, **2** and **3** were synthesized by one-step method i.e. by the Pd-catalyzed Buchwald-Hartwig cross-coupling reaction [24] between 5-bromo-3-(9-ethyl-9*H*-carbazol-3-yl)-2-methylquinazolin-4(3*H*)-one (**2a**) and 3,6-di-*tert*-butyl-9*H*-carbazole (**3a**), 4,4'-di-*tert*-butyl-diphenylamine or 4,4'-dimethoxydiphenylamine. Compound **4** was synthesized by Heck reaction of **2a** with 9-ethyl-3-vinyl-9*H*-carbazole (**3c**) in the presence of palladium(II) acetate and tri-*o*-tolylphosphine. Compound **5** was obtained via Suzuki cross-coupling reaction of **2a** with 2-(*N*-methylcarbazol-3-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (**3b**). The synthesized compounds were purified by column chromatography and recrystallization. The yields ranged from 42 to 64%. The chemical structures were confirmed by IR-, ¹H NMR, ¹³C NMR and mass spectrometries as well as by elemental analysis. The obtained compounds exhibited good solubility in common organic solvents such as dichloromethane, chloroform, chlorobenzene, toluene.



Scheme 1. Synthetic routes to 1-5.

3.2. Geometries and molecular orbitals

Carbazolyl-substituted quinazolinones **1-5** were studied using quantum chemical calculations. The optimized geometries and frontier orbitals of the isolated molecules are presented in Fig 1. In these compounds carbazole attached at N atom of quinazolinone form torsion angle of $87-93^{\circ}$ with central fragment. In the case of molecules **1**, **4** and **5**, the size of torsion angles between the planes of the second carbazole and quinazolinone moieties are different. Carbazole with central fragment show torsion angles of 53° and 37° in **1** and **5**, respectively, while compound **4** having ethenyl-containing linkage demonstrate flat configuration. The torsion angles between phenyl rings and quinazolinone moiety in the structures of **2** and **3** are in the range of $40-48^{\circ}$. The determined geometries of **1-5** lead to the HOMO distribution on the quinazolinone moiety and the different donor substituents. The

electron density of LUMO in 2, 3 and 5 is predominantly localized on the ethyl-carbazole unit, while in 1 electron cloud is shifted to the quinazolinone moiety. Only compound 4 has the similar LUMO distribution as that of HOMO i.e. the LUMO is localized on the quinazolinone moiety extending on the conjugated double bond linkage and ethyl-carbazole.

<Insert Figure 1>

3.3. Thermal properties

The thermal stabilities of the compounds were estimated by TGA under a nitrogen atmosphere. The 5% weight loss temperatures ($T_{dec-5\%}$) of **1-5** are summarized in Table 1. TGA curves are shown in the Supporting Information (Fig. S1, SI).

<Insert Table 1>

 $T_{dec-5\%}$ of the compounds were found to be rather high and ranged from 418 to 437 °C. 4,4'-Di*tert*-butyl-diphenylamino- and 4,4'-di-methoxydiphenylamino-substituted compounds 2 and 3 exhibited higher thermal stability than 3,6-di-*tert*-butylcarbazolyl-substituted quinazolinone 1. Compound 4 having 9-ethyl-3-vinylcarbazyl substituent showed the lowest 5% weight loss temperature.

Quinazolinones 1-5 were isolated after the synthesis as the crystalline substances. However, they could be transformed into molecular glasses by cooling their melts as it was confirmed by DSC. DSC thermograms of compound 2 are shown in Fig. 2.

<Insert Figure 2>

When the sample of **2** was heated during DSC experiment the endothermal melting signal was observed at 297 °C. The cooling scan did not show any signal of crystallization. The following heating scan revealed only the glass transition at 154 °C. The similar behavior in DSC experiments was observed for compounds **1**, **3-5**. In the first heating scans compounds **1**, **3-5** showed endothermic melting signals at 224, 242, 269 and 260 °C, respectively. In the repeated heating scans these compounds showed only glass transitions at 132, 146, 157 and 159 °C, respectively. High T_g values of compounds **1-5** allow to predict high morphological stability of their molecular glasses. T_g of compounds **4** and **5** having 9-ethyl-3-ethenylcarbazolyl and *N*-methylcarbazolyl substituents, respectively, was found to be higher by 25 and 27 °C than that of compound **1** with 3,6-di-*tert*-butyl carbazolyl donor substituent. Apparently *tert*-butyl groups present in compound **1** ensure plasticizing effect of its glass. T_g of compound **2** containing *tert*-butyl groups at the 4,4'-positions of the diphenylamino moiety was found to be higher by 8 °C than that of compound **3** with methoxy groups at the 4,4'-positions of the diphenylamino moiety. This observation can apparently be explained by the higher molar mass of compound **2**, which results in the stronger intermolecular interaction in the glassy state.

3.4. Optical and photophysical properties

UV absorption and fluorescence (FL) spectra of dilute THF solutions of **1-5** are shown in Fig. 3. The wavelengths of low-energy absorption and emission maxima of the solutions and the solid films, Stokes shifts are summarized in Table 2. The TDDFT calculations in gas phase were performed to identify low-energy transitions in the absorption spectra of compounds **1-5** (Table S1).

<Insert Table 2>

<Insert Figure 3>

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The profiles of absorption spectra of compounds 1-5 were found to be similar. The theoretical absorption spectra (Fig. S2) indicate that low energy excitations $(S_0 \rightarrow S_1, S_0 \rightarrow S_2)$ of 1, 2, 3 and 5 have charge transfer (CT) character. These excitations are mainly contributed by the transitions HOMO \rightarrow LUMO, LUMO+1, LUMO+2. In the case of compound 4, $S_0 \rightarrow S_1$ corresponds to the transition in the same 9-ethyl-3-ethenylcarbazolyl and quinazolinone moieties. This transition characterizes the lowest energy absorption band of 4 which is red-shifted in respect to those of compounds 1-3 and 5 (Fig. 3a). The results obtained show that compound 4 has more extended conjugated π -electron system due to the presence of ethenyl-linkage.

From the spectroscopic absorption edge (λ_{edge}^{a} , nm), the optical band gap (\mathbf{E}_{g}^{opt}) values were estimated according to the formula \mathbf{E}_{g}^{opt} =1240/ λ_{edge}^{a} [25], and were found to range in the order: 1 > 5 >2 > 3 > 4 (Table 4). FL spectra of the dilute solutions of 1-5 are characterized the single peaks with the intensity maxima in the range of 403-483 nm. Fig. 3c displays fluorescence decay curves of the dilute THF solutions of the studied compounds recorded at the fluorescence band maxima. The fluorescence transients of the dilute THF solutions of the compounds can be well described by the single exponential functions with the lifetimes (τ) ranging from 0.91 to 6.47 ns (Table 3). Both bathochromic shift of FL spectrum and longer lifetime observed for compound **3** can be explained by more twisted molecular structure in the excited state, compared with those observed for the other compounds. The shortest τ (0.91 ns) obtained for compound **4** that was characterized by higher fluorescence quantum yield ($\Phi_{\rm F}$) (Table 2) can apparently be explained by enhanced π -electron delocalization due to more planar molecular structure of **4** (dihedral angle between the quinazolinone and 9-ethyl-3-vinylcarbazolyl moieties of 1°, Fig. 1).

<Insert Figure 4>

Fig. 4 shows the normalized absorption and emission spectra of the solid films of compounds 1-5. The absorption spectra are slightly red-shifted as compared with the corresponding spectra of the dilute solutions. This observation can be explained by the intermolecular interaction, which takes place in the films [26]. The emission maxima of the solid samples of 1-5 were found to be in the range from 411 to 485 nm with the excitation wavelength of 350 nm.

<Insert Table 3>

The FL spectrum of the solid layer of 1 was very similar to these recorded for dilute THF solution of 1; while the FL spectra of the solid layers of 4-5 were found to be slightly red-shifted compared to FL spectra of the solutions of the compounds apparently due to intermolecular interactions (Fig. 3b and 4b). FL spectra of the solid samples of most of the compounds, except that of compound 5 were similar to those of dilute solutions, which implied the low probability of the formation of excited dimers of compounds in the solid state. Fl spectrum of the solid film of compound 5 had a shoulder at ca. 490 nm (Fig. 4b) which can be assigned to the formation partially overlapped excimers.

PL decay transients for the solid layers of compounds 1-5 were also recorded (Fig. S3). Doubleexponential fits were used for the statistical representation of the decay curves (χ^2 values were not higher than 1.3). The lifetimes with the different fractional intensities are summarized in Table 3. The lifetimes of the first (fast) time decay components were found to be lower than those recorded for dilute THF solutions of 1-5 (Table 3). The different values of dielectric constant of both the media and the intermolecular interactions in the solid state could be the reasons of this observation. The longerlived decay components observed for compounds 1-5 can probably be associated with the formation of the intermolecular excimers in the layers. This assumption is supported by the observation that the solid-state PL spectra of compounds 1-5 are broader than those of THF solutions. The solid-state PL spectrum of 5 even contains shoulder (Fig. 4b) [27]. In addition, the slow decay components could be

explained by the excitation migration towards the non-radiative decay sites and/or by the crystalline aggregate formation in the neat films [28].

The Stokes shifts recorded for the dilute THF solutions of compounds **1-5** ranged from 48 to 134 nm, while those observed for the solid films were similarly in the range of 46-113 nm. The highest Stokes shift of the dilute solution of **3** can apparently be explained by the most considerable difference of the conformations of the ground and excited states. The small Stokes shifts observed both for the dilute solution and for the solid sample of **4** provides the information on the small changes in geometry after excitation.

Compounds 1-3 and 5 due to their non-planar structure, apparently, exhibited photoinduced charge transfer (CT) character in excited state. Therefore, the dilute THF solutions and solid films of these compounds suffered from CT caused fluorescence quenching [29]. The solutions of compounds 1-3 and 5, showed rather low values of Φ_F ranging from 5.8 to 12.2% (Table 2). Even lower Φ_F ranging from 0.4 to 1.7% were recorded for the condensed state due to aggregation induced quenching. Compound 4 having rigid structure demonstrated relatively high fluorescence quantum yield (44.3%) in dilute solution. However, the π - π stacking interactions of planar molecules of 4 in the solid state induced non-radiative energy transfer, resulting in self-quenching of fluorescence [30]. Φ_F of the solid sample of 4 was found to be 1.1%.

The rigid structure of compound **4** brought about relatively high fluorescence quantum yield (Φ_F) of 44.3% for the dilute solution of the compound.

The photoluminescence (PL) and phosphorescence (Ph) spectra of the dilute solutions of the studied compounds in THF recorded at liquid nitrogen temperature (77 K) are presented in Fig. 5. The substitution mode was found to have influence on the phosphorescence spectra and triplet-energy levels (E_T) of compounds 1-5. Intense triplet emission was observed at low temperatures for compounds 1-3 and 5 with 4,4'-di-*tert*-butyl-diphenyl, 3,6-di-*tert*-butylcarbazolyl and *N*-methylcarbazolyl substituents, respectively (Fig. 5). However, the intensity of phosphorescence emission for compound 4 was very low displaying extremely low quantum yield of phosphorescence

of the compound. For this reason it was impossible to record phosphorescence spectrum of the solution of **4** at the used gate (> 50 ms). The singlet- and triplet-energy levels (E_{S1} and E_{T1}) were determined from the onsets of the fluorescence and phosphorescence spectra, respectively (Table 4, Fig. 5).

<Insert Figure 5>

<Insert Table 4>

3.5. Electrochemical and electron photoemission properties

In order to investigate the electrochemical properties of the molecules (1-5), CV measurements were performed at 25 °C for DCM solutions. The CV profiles of compound 4 are shown in Fig. 6 as an example. The electrochemical potentials and energy levels are summarized in Table 5.

<Insert Figure 6>

<Insert Table 5>

As shown in Fig. 6a, compound **4** exhibited two quasi-reversible oxidation processes. No reduction waves were detected. The first oxidation peak corresponds to the removal of electrons from the carbazolyl group, resulting in radical cations. Compound **4** is very sensitive towards electrochemical oxidation due to the electron-rich and highly activated 3,3'-positions of two carbazole moieties. Their repeated CV scans display an increasing change in the CV traces, proving that a series of electro-polymerization reactions [31] of the radical cation species take place on the glassy carbon electrode surface in the potential range 0-1.4 V. The similar quasi-reversible oxidation processes,

electrochemical polymerization and the film formation on the electrode surface were observed for the CVs profiles of **2-5** (Fig. S4). It is worth of noting that the first oxidation peaks of **2**, **3** and **4** occured at a lower potentials than that of **1**, **5** (Table 5). This observation is in agreement with the UV spectrometry data. The low-energy absorption bands of **2**, **3** and **4** appeared at lower energies than those of **1** and **5**.

DPV spectra (Fig. 6b) of compounds **1-5** show absolute peaks of oxidation processes. The first oxidation potential peaks of carbazolyl-substituted quinazolinones **1** (1.02 V), **4** (0.69 V) and **5** (0.76 V) are at a higher potentials than those of 4,4'-di-*tert*-butyl-diphenylamino- or 4,4'-di-methoxyphenylamino-substituted quinazolinones **2** (0.64 V) and **3** (0.53 V).

Although other approaches were used to calculate the solid state ionization potential (IP_{CV}) based on electrochemical data [32], the conversion reported by the Forrest group [33] has a better correlation between electrochemical data and ionization potential and afforded a better fit between optical bandgap. According to the method reported by Forrest et al [33], IP_{CV} value is calculated using the equation IP_{CV} = $|-(1.4 \times 1e \times \frac{E_{onset}^{ox}}{e^{osset}} \text{ vs Fc/V}) - 4.6|$ eV. The electron affinity (EA_{CV}) was obtained from the equation: EA_{CV} = $-(|IP_{CV}| - \frac{E_g^{opt}}{e^{ost}})$. The values of EA_{CV} were found to range from -2.24 to -1.68 eV. The values of IP_{CV} are given in Table 5. They ranged from 5.03 eV for **3** to 5.43 eV for **1**.

Ionization potentials (IP_{PE}) of the solid layers of compounds **1-5** were estimated by photoelectron emission spectroscopy. Photoelectron emission spectra are shown in Fig. 7.

<Insert Figure 7>

The intersection points of the linear parts of the photoelectron spectra drawn with the abscissa axis gave the ionization potential values. IP_{EP} values of derivatives **1-5** ranged from 5.35 to 5.66 eV (Table 5). While the IP_{EP} values are slightly larger than the corresponding ones obtained by CV

 (IP_{CV}) , both methods indicate the same tendencies. Carbazolyl-substituted quinazolinones 1, 4 and 5 exhibited a little higher ionization potentials than diphenylamino-substituted compounds 2 and 3.

3.6. Charge-transporting properties and performance in phosphorescent OLED

Time of flight measurements were used for the estimation of charge-transporting properties of compounds 1-5. Fig. 8a displays the electric field dependencies of hole mobilities for the layers of these compounds. The hole mobility values of 1-5 were in the range between 10^{-4} and 10^{-3} cm²/V·s at high electric fields. The best charge transport properties were observed for the layer of compound 2. It showed hole drift mobility of 1.1×10^{-3} cm²/Vs at an electric field of 8.1×10^5 V/cm. The hole mobilities for all the studied compounds were strongly dependent upon electric field. The photocurrent profiles of hole carrier transport for 2 showed a low-dispersive behavior with a plateau and subsequent drop (Fig. 8b). A dispersive behavior was found for the photocurrent profiles of hole transport for 1, 3-5. These results indicate that hole transport is limited by bulk trapping for 1, 3-5, whereas the hole transport is less influenced by this effect for 2.

Insert Figure 8>

Compound **2**, which showed relatively high triplet level and hole transport with the lowdispersity, was tested as a host in green (device A) and blue (device B) phosphorescent OLEDs. Simple OLED structures were chosen utilizing 4,4',4''-tris[phenyl(*m*-tolyl)amino]triphenylamine (*m*-MTDATA) and 4,7-diphenyl-1,10-phenanthroline (Bphen) for the hole- and electron-injecting layers, respectively (Fig. S5). Tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)₃) and bis[2-(4,6difluorophenyl) pyridinato-C2,N](picolinato)iridium(III) (FIrpic) were exploited as green and blue dopants in the fabricated phosphorescent OLEDs, respectively (Fig. S5).

Electroluminescence (EL) spectra of the devices A and B are shown in Fig. 9a. EL spectra of the device A recorded at the different applied voltages are characterized by green emission with the intensity maximum at *ca*. 516 nm, confirming the radiative recombination of excitons on $Ir(ppy)_3$ [34]. The green device A demonstrated the relatively low value of the turn-on voltage of ca. 3.0 V as well as the relatively high values of maximum power and external quantum (EQE) efficiencies of ca. 23.2 lm/W and 7.1%, respectively (Fig. 9c,d). Blue emission with the intensity maxima at ca. 478 nm of the device B at the different applied voltages was observed. The EL spectra of device B were much broader compared to the FIrpic emission showing that the radiative recombination of excitons occurred on both FIrpic and host 2 [35]. It is understandable since HOMO of FIrpic is much lower compared to HOMO of host 2 providing the energy barer for holes (Fig. 9b). Therefore, the radiative recombination on host 2 was also possible affecting not only EL spectra but also output characteristics of device B (Fig. 9c,d). In addition, low performance of device B can be explained by the usage of hole- and electron-transporting layers with low triplet energy levels of 2.67 eV for *m*-MTDATA and 2.5 eV for Bphen as compared to 2.7 eV for FIrpic resulting in inefficient triplet exciton harvesting by the blue phosphorescent emitter. Therefore, the structure of device B was modified by adding the layer of 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) with triplet energy of 2.87 eV as the hole-transporting and exciton-blocking layer and the layer of diphenyl-4triphenylsilylphenyl-phosphineoxide (TSPO1) with triplet energy of 3.36 eV as hole-blocking, electron-transporting and exciton-blocking layer. 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-Hbenzimidazole) (TPBi) was employed for the preparation of electron-transporting (ET) layer (Fig. S5). Practically, new device C was fabricated with the following structure ITO/m-MTDATA(30 nm)/TAPC(8 nm)/2:FIrpic(30 nm)/TSPO1(8 nm)/TPBi(30)/Ca:Al. The energy energy diagram of device C is present in Fig. 9b. The characteristics of device C were better than those of device B (Fig. 9c,d) but "white" EL of device C was far from blue emission of FIrpic (Fig. 9a). The high-energy band of EL spectrum of device C was sufficiently similar to that of device B and it can be explained by the same reasons. Low-energy band with the maximum at 588 nm can be attributed to electroplex

of TAPC as this band is not observed neither in PL spectra of pure materials used in the device or in the spectra of their solid-state mixtures. Thus, compound 2 is not exciplex-forming material as, for example, 3-(2,7-dicyanocarbazol-9-yl)-9-ethylcarbazole [36]. The similar band was previously observed in EL spectra of TAPC-based OLEDs [37]. In device D, TAPC was replaced by the layer of compound **2**. EL spectrum of devcice D practically originates from FIrpic emitter. This device exhibits higher performance than devices B and C (Fig. 9). The blue device D is characterized by the turn-on voltage of *ca*. 5.1 V, maximum power efficiency of ca. 11 lm/W and external quantum efficiency (EQE) of ca. 6.9% (Fig. 9c,d). The characteristics of the fabricated and characterized OLEDs show that quinazolinone-based compound **2** with relatively high triplet level and holetransporting property can be used for the fabrication electroluminescent devices. The similar behaviours were observed for the quinazolinone-based compound **1**, **3-5** which were studied in the structures of devices C and B replacing compound **2** in the light-emitting layer. The data of electroluminescence study of compounds **1**, **3-5** are presented in the SI (Fig. S6).

<Insert Figure 9>

4. CONCLUSIONS

Five quinazolinones with the different substitution pattern were synthesized and their thermal, optical, photophysical, electrochemical, photoelectrical, and electroluminescent properties were investigated. All the synthesized compounds formed glasses with the glass transition temperatures ranging from 97 to 159 °C. The 5% weight loss temperatures of the compounds were found to be rather high and ranged from 397 to 451 °C. The theoretical absorption spectra indicate that low energy excitations ($S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$) of the synthesized compounds have charge transfer character. Only 3-(9-ethyl-9*H*-carbazol-3-yl)-5-((E)-2-(9-ethyl-9*H*-carbazol-3-yl)ethenyl)-2-methylquinazolin-4(3H)-one has the similar LUMO distribution as that of HOMO i.e. the LUMO is localized on the quinazolinone

moiety extending on the conjugated double bond linkage and ethyl-carbazole. Fluorescence quantum yields of dilute THF solutions of the synthesized materials ranged from 7.8 to 44.3%. The highest value of triplet-energy of 2.99 eV was found for 5-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3-(9-ethyl-9Hcarbazol-3-yl)-2-methylquinazolin-4(3H)-one. Dilute THF solutions of the compounds exhibited a single exponential fluorescence decays with lifetimes ranging from 0.91 to 6.47 ns. The ionization potentials of the films of the quinazolinone-based derivatives measured by the photoelectron emission spectrometry ranged from 5.35 to 5.66 eV. The ionization potential values estimated by cyclic voltammetry ranged from 5.03 to 5.43 eV and electron affinity values ranged from -2.24 to -1.68 eV. All the synthesized compounds were found to be capable of transporting holes. The layers of most of the compounds showed dispersive hole transport while that of 5-(bis(4-tert-butyldiphenyl)amino)-3-(9-ethyl-9H-carbazol-3-yl)-2-methylquinazolin-4(3H)-one was characterized by low-dispersity hole transport. Time-of-flight hole mobilities in the layer of this material reached 1.1×10^{-3} cm²/Vs at an electric field of 8.1×10^5 V/cm at the room temperature. Utilizing this compound as the host, green and blue phosphorescent organic light emitting diodes with turn-on voltage of ca. 3.0 and 5.1 V, maximum power and external quantum efficiencies of ca. 23.2 and 11 lm/W and 7.1 and 6.9%, respectively were fabricated.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org.

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Scheme 1. Synthetic routes to 1-5.

Table 1. Thermal characteristics of quinazolinone derivatives 1-5.

Table 2. Photophysical properties of the dilute THF solutions and of the solid films of compounds 1-

5.

Table 3. Photoluminescence decay parameters of 1-5 compounds.

Table 4. Excited states energies of compounds 1-5.

Table 5. The values of oxidation potentials, optical band gap energies, IP_{PE} , IP_{CV} , EA_{CV} for compounds 1-5.

Figure 1. The optimized geometries and frontier orbitals of compounds 1-5 obtained at the B3LYP/6-

31G(d,p) level in gas phase.

Figure 2. DSC thermograms of compound 2 (scan rate of 10 °C/min, N₂ atmosphere).

Figure 3. Normalized UV (a) and FL (b) spectra ($\lambda_{ex} = 330$ nm) and fluorescence decay curves recorded at the fluorescence band maxima (c) of the dilute THF solutions (10⁻⁵ M) of compounds 1-5. Figure 4. Normalized UV (a) and FL (b) spectra ($\lambda_{ex} = 350$ nm) of the solid films of compounds 1-5. Figure 5. Normalized photoluminescence (thin dashed curves) and phosphorescence (thick solid curves) spectra of compounds 1-5 in THF solutions at 77 K.

Figure 6. (a) Repetitive anodic sweeps at a platinum electrode in a 0.1 M Bu_4NBF_6/DMC electrolyte solution of compound 4. (b) Differential pulse voltammperometric (DPV) curves of 1mM of compound 4 in 1M Bu_4NBF_6/DCM electrolyte.

Figure 7. Photoelectron emission spectra of the solid films of compounds 1-5 recorded in air.

Figure 8. Electric field dependencies of hole mobilities for the layers of compounds 1-5 (a). TOF transients at different electric fields in the log-log and the linear (insets) scales for the layer of compound 2 (b).

Figure 9. EL characteristics of devices A, B, C and D: a) EL spectra recorded at the different applied voltages; b) energy-band diagrams; c) current density and luminance versus voltage d) power and external quantum efficiencies versus current density.

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Compound	$T_{g}/^{o}C^{[1]}$	$T_m / {^\circ C^{[1]}}$	T _{dec-5%} /°C ^[2]
1	132	224	426
2	154	297	434
3	146	242	432
4	157	269	418
5	159	260	437

Table 1. Thermal characteristics of quinazolinone derivatives 1-5.

^[1] T_m – melting temperature; T_g – glass transition temperature, scan rate 10 °C/min, N₂ atmosphere. ^[2] $T_{dec-5\%}$ – 5% weight loss temperatures, scan rate 20 °C/min, N₂ atmosphere.

	Solution in THF					Se	olid film	
р								
npour	$\lambda_{abs}^{[a]}$ /	$\lambda_{F}^{\max[b]}$ /	$\Phi_F^{[c]}$ /	Stokes shift /	$\lambda_{abs}^{[a]}$ /	$\lambda_{F}^{\max[b]}$ /	$\Phi_F{}^{[d]}/$	Stokes shift /
Coi	nm	nm	%	nm	nm	nm	%	nm
1	342	415	5.8	73	350	411	1.7	61
2	347	446	6.1	99	351	464	1.2	71
3	349	483	7.8	134	372	485	0.6	113
4	383	431	44.3	48	391	438	1.1	46
5	347	403	12.2	56	355	410	0.4	65

 Table 2. Photophysical properties of the dilute THF solutions and of the solid films of compounds 1

5.

^[a] Peak wavelength of lowest energy absorption bands. ^[b] Wavelength of fluorescence band maximum. ^[c] Fluorescence quantum yield of solution. ^[d] Fluorescence quantum yield of solid film.

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Compound	Solution	Solution in THF		Solid-state films		
	τ [ns]	χ ²	τ_1 [ns]	$\tau_2 [ns]$	χ ²	
1	3.54	1.077	3.14 (73%)	9.42 (27%)	1.269	
2	4.10	1.101	3.87 (69%)	10.45 (31%)	1.298	
3	6.47	1.217	3.69 (54%)	10.68 (46%)	1.200	
4	0.91	1.069	0.61 (92%)	3.19 (8%)	1.005	
5	3.58	1.128	0.83 (69%)	3.03 (31%)	1.088	

Table 3. Photoluminescence decay parameters of 1-5 compounds.

Photoluminescence decays were recorder at the PL maximum.

Table 4. Excited states energies of compounds 1-5.

Compound		Energy (eV)	
Compound	E _{S1}	E _{T1}	ΔE_{ST}
1	3.36	2.99	0.37
2	3.05	2.67	0.38
3	2.91	2.53	0.38
4	3.14	-	-
5	3.45	2.72	0.73
)		

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Compound	E_{onset}^{ox} VS $E_{C}/V^{[a]}$	IP _{CV} /eV ^[b]	EA _{CV} /eV ^[c]	$\mathrm{E}^{_{g}}_{_{g}}/\mathrm{eV}^{[\mathrm{d}]}$	IP _{PE} /eV ^[e]
	10/ 1			4	
1	0.63	5.43	-1.89	3.54	5.66
2	0.33	5.13	-1.78	3.35	5.38
3	0.23	5.03	-1.68	3.35	5.35
4	0.39	5.19	-2.24	2.95	5.42
5	0.46	5.26	-1.83	3.43	5.58

Table 5. The values of oxidation potentials, optical band gap energies, IP_{PE} , IP_{CV} , EA_{CV} for compounds **1-5**.

^[a] E_{onset}^{ox} is oxidation potential measured *vs.* ferrocene/ferrocenium. ^[b] IP_{CV} is ionization potential. ^[c] EA_{CV} is electron affinity. ^[d] E_{g}^{opt} is the optical energy gap. ^[e] Ionization potentials estimated by photoelectron emission spectrometry.

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31G(d,p) level in gas phase.



Figure 2. DSC thermograms of compound 2 (scan rate of 10 °C/min, N₂ atmosphere).



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external quantum efficiencies versus current density.

ACCEPTED MANUSCRIPT Supporting Information

Carbazolyl-substituted quinazolinones as high-triplet-energy materials for

phosphorescent organic light emitting diodes

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Figure S1. TGA curves of 1-5 recorded at the heating rate of 20 $^{\circ}$ C/min in N₂.

ACCEPTED MANUSCRIPT **Table S1.** Theoretical optical characteristics of compounds 1–5.

Compound	Transition	Excitation energy, nm	$f^{[a]}$	Transition configuration	
1	$S_0 \rightarrow S_1$	365	0.0113	H→L (97%)	
I	$S_0 \rightarrow S_2$	342	0.3633	H→L+2 (91%)	~
	$S_0 \rightarrow S_1$	376	0.0233	H→L+1 (95%)	
2	$S_0 \rightarrow S_2$	357	0.0060	H→L (97%)	
	$S_0 \rightarrow S_3$	346	0.6414	H→L+2 (96%)	
	$S_0 \rightarrow S_1$	390	0.0167	H→L+1 (95%)	
3	$S_0 \rightarrow S_2$	373	0.0013	H→L (97%)	
	$S_0 \rightarrow S_3$	351	0.6282	H→L+2 (97%)	
4	$S_0 \rightarrow S_1$	378	1.33	H→L (92%)	
	S₀→S1	328	0.0188	H→L+1 (26%)	
5				H→L+2 (58%)	
	$S_0 \rightarrow S_2$	323	0.4648	H→L+2 (66%)	

a Oscillator strength.



Figure S2. The theoretical spectra obtained by mean of TDDFT calculations in gas phase.



Figure S3. Fluorescence decay curves recorded at the fluorescence band maxima (Table 2) of the

solid films of compounds 1-5.



Figure S4. Repetitive anodic sweeps at a platinum electrode in a 0.1 M Bu₄NBF₆/DCM electrolyte

solutions of compounds 1-3, 5.



BPhen





Figure S5. The structures used materials for the OLED constructions.



b)



Figure S6. Figure 9. EL characteristics: a) EL spectra recorded at the different applied voltages; b) current density and luminance versus voltage; c) external quantum efficiencies versus current density of devices C1, C3, C4, and C5 with structures ITO/*m*-MTDATA(30 nm)/TAPC(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/TPBi(30)/Ca:Al as well as devices D1, D3, D4, and D5 with structures ITO/*m*-MTDATA(30 nm)/**Z**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/**2**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/**2**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/**Z**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/TSPO1(8 nm)/**Z**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/TSPO1(8 nm)/**Z**(8 nm)/**1**, **3**, **4**, or **5**:FIrpic(30 nm)/TSPO1(8 nm)/TS

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

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Highlights

- Derivatives of carbazolyl-substituted quinazolinones were synthesized.
- Their glass transition temperatures ranged from 97 to 159 °C.
- Hole mobilities values were up to 10^{-3} cm²/V·s at electric field of 8.1×10⁵ V/cm.
- Green and blue phosphorescent organic light emitting diodes showed efficiencies of 7.1 and 6.9%, respectively.