



## Efficient synthesis and structural effects of ambipolar carbazole derivatives



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### ABSTRACT

A new class of carbazole derivatives, with varying degree of core substitution was synthesized and characterized. The presented synthetic route requires mild conditions, starts from low-cost substrates and leads to the formation of the target products with good yields. The optical and electronic properties of the synthesized materials were estimated and supported by DFT calculations. Investigated compounds emit violet light with quantum efficiency reaching 18.2%. Electrochemical and electron photoemission spectroscopy revealed that ionization potentials are in range of 5.10–5.30 eV. Time-of-flight measurements revealed that those compounds have balanced hole and electron mobility in range of  $4.27 \cdot 10^{-6}$ – $8.42 \cdot 10^{-5}$  cm<sup>2</sup>/Vs for star-shaped compound and  $6.2 \times 10^{-7}$ – $6.2 \times 10^{-6}$  cm<sup>2</sup>/Vs for linear derivatives. Electroluminescence spectra of the OLED device prepared using the newly synthesized compounds were characterized by broad emission in visible range, resulting in white light generation.

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### 1. Introduction

Recent years have seen a constant increase of interest in carbazole-based molecules for optoelectronics. Among them, molecules with star-shaped architecture gain particular attention, owing to their properties that distinguish them from their linear analogues [1]. The main drawback of star-shaped materials is however, their complex synthesis [2]. Many reported compounds are obtained with low yields. Moreover, such compounds require multistep synthesis or use of expensive substrates. Taking these factors into consideration, the synthesis of star-shaped compounds becomes the stage limiting the possibility of wide applications of these systems.

The increased interest in carbazole as a building unit of organic  $\pi$ -conjugated materials is associated with their unique properties. The connection of carbazoles through the 2,7-positions ensures extension of  $\pi$ -conjugation, while the connection through the 3,6-

positions enhances the donor ability [3]. Numerous papers report carbazole derivatives for application in organic light emitting diodes (OLEDs), in which those materials fulfill different functions. For example, carbazoles are known for their blue fluorescence and hence, find application as emitting materials [4–6]. In addition, carbazole derivatives are also used as host materials for high quantum efficiency phosphorescent OLEDs [7–10], due to their high triplet energy, combined with the precluding of formation of  $\pi$ -stacks [11,12]. Some carbazole-based materials exhibit aggregation-induced emission enhancement [13]. Delayed fluorescence of carbazole derivatives is of special interest [14,15]. This can be observed from intra-molecular excited states and from exciplexes [16,17]. The mixed emission from excitons and exciplexes can lead to a variety of colors. The exciplex emission of blue, green or orange colors was already reported [18–20]. This phenomenon in turn, can be exploited in the fabrication of white OLEDs which are of special interest [21–23]. The use of multifunctional molecules can allow to improve OLED performance [24].

Herein, the synthesis and characterization of a new group of carbazole-based compounds for inter-molecular D-A systems is presented. Our series of compounds was synthesized by the attachment of one, two or three carbazole units to melamine core. Photophysical properties were investigated.

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## 2. Experimental

### 2.1. Materials

Carbazole (TCI), potassium hydroxide (Fluka), 1-iodooctane (Acros Organics),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Acros Organics), acetic anhydride (POCH, Gliwice, Poland) acetic acid (POCH, Gliwice, Poland), hydrazine hydrate, Pd/C (10%, unreduced, Acros Organics),  $\text{K}_2\text{CO}_3$  (Acros Organics) were used as received. 2-Chloro-4,6-dimethoxy-1,3,5-triazine and 2,4-dichloro-6-methoxy-1,3,5-triazine were synthesized according to procedures described earlier [25,26]. Tetrahydrofuran (THF) (Acros) was distilled prior to use and kept under molecular sieves. Dimethyl sulfoxide (DMSO) (Fisher Scientific) was used as received and kept under molecular sieves.

#### 9-Octyl-9H-carbazole

Synthesis according to known procedure [27]. To a solution of carbazole (9.42 g, 56.45 mmol) in 50 ml of DMSO, potassium hydroxide (3.17 g, 56.45 mmol) was slowly added over ten minutes. The solution was then stirred for 15 min., after which 1-iodooctane (12.9 g, 53.76 mmol, 9.7 ml) was added dropwise over twenty minutes. After reacting the mixture for seven hours, it was poured into water (300 ml), extracted with chloroform ( $3 \times 50$  ml) and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane:chloroform 6:1, v/v) to afford viscous liquid of 9-octyl-9H-carbazole. Yield was equal to 86% (12.87 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.09 (ddd,  $J = 7.8, 1.2, 0.8$  Hz, 2H, ArH), 7.51–7.41 (m, 2H, ArH), 7.41–7.34 (m, 2H, ArH), 7.28–7.15 (m, 2H, ArH), 4.27 (t,  $J = 7.3$  Hz, 2H,  $\text{N}-\text{CH}_2-$ ), 1.85 (q,  $J = 7.2$  Hz, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.44–1.12 (m, 10H, CH aliphatic), 0.86 (t,  $J = 6.6$  Hz, 3H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.57, 125.68, 122.96, 120.46, 118.81, 108.78, 43.21, 31.94, 29.52, 29.32, 29.11, 27.47, 22.75, 14.20.

#### 3-Nitro-9-octyl-9H-carbazole

Modification of known procedures [28,29]. 9-octyl-9H-carbazole (2.58 g, 9.25 mmol) was dissolved in a mixture containing 20 ml of acetic anhydride and 20 ml of acetic acid. The resulting solution was stirred for 15 min., after which  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1.12 g, 4.26 mmol) was added portionwise during 20 min. Reaction was carried for one hour, during which a large amount of yellow precipitate was formed. Reaction was quenched by pouring it into 500 ml of distilled water, followed by collection of yellow precipitate by filtration and washing it thoroughly with distilled water. Residue was purified by column chromatography (hexane:chloroform 1:1, v/v) to afford yellow solid of 3-nitro-9-octyl-9H-carbazole. Yield was equal to 78% (2.35 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.96 (d,  $J = 2.3$  Hz, 1H, ArH), 8.35 (dd,  $J = 9.1, 2.3$  Hz, 1H, ArH), 8.11 (d,  $J = 7.8$  Hz, 1H, ArH), 7.61–7.50 (m, 1H, ArH), 7.45 (d,  $J = 8.2$  Hz, 1H, ArH), 7.40–7.29 (m, 2H, ArH), 4.30 (t,  $J = 7.3$  Hz, 2H,  $\text{N}-\text{CH}_2-$ ), 1.87 (q,  $J = 6.9$  Hz, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.47–1.13 (m, 10H, CH aliphatic), 0.85 (t,  $J = 6.7$  Hz, 3H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.73, 141.85, 140.78, 127.60, 123.06, 122.76, 121.80, 121.19, 120.95, 117.51, 109.93, 108.45, 43.84, 32.00, 29.54, 29.38, 29.16, 27.49, 22.84, 14.31. M.p.: 82 °C (lit. [30] 85 °C)

#### 9-Octyl-9H-carbazol-3-amine

Modification of known procedures [28,29]. A solution of 3-nitro-9-octyl-9H-carbazole (2 g, 6.16 mmol) and Pd/C (10% w/w) (0.01 g) in 120 ml of ethanol was heated to reflux for 15 min. To this solution, 6 ml of hydrazine hydrate was added dropwise over one hour. Under the temperature of reflux, the reaction was carried overnight. Afterwards, Pd/C was filtered off and the solvent was removed under reduced pressure. Residue was purified by column chromatography (hexane:ethyl acetate 2:1, v/v +1% triethylamine) to afford lightly brown solid of 9-octyl-9H-carbazol-3-amine. Yield was equal to 84% (1.52 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.99 (ddd,  $J = 7.8, 1.2, 0.7$  Hz, 1H, ArH), 7.45–7.37 (m, 2H, ArH), 7.36–7.31 (m,

1H, ArH), 7.21 (dd,  $J = 8.5, 0.5$  Hz, 1H, ArH), 7.17–7.11 (m, 1H, ArH), 6.90 (dd,  $J = 8.5, 2.3$  Hz, 1H, ArH), 4.22 (t,  $J = 7.2$  Hz, 2H,  $\text{N}-\text{CH}_2-$ ), 3.61 (s, 2H, Ar- $\text{NH}_2$ ), 1.82 (q,  $J = 7.2$  Hz, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.40–1.17 (m, 10H, CH aliphatic), 0.86 (t,  $J = 6.6$  Hz, 3H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.16, 139.10, 135.31, 125.64, 123.80, 122.59, 120.56, 118.19, 115.78, 109.46, 108.81, 106.51, 43.38, 32.06, 29.65, 29.44, 29.29, 27.59, 22.86, 14.32. M.p.: 65–66 °C (lit. [30] 65 °C)

#### N-(4,6-dimethoxy-1,3,5-triazin-2-yl)-9-octyl-9H-carbazol-3-amine (1CM)

A solution of 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.20 g, 1.15 mmol), 9-octyl-9H-carbazol-3-amine (0.34 g, 1.15 mmol) and  $\text{K}_2\text{CO}_3$  (0.16 g, 1.15 mmol) in 25 ml of THF was heated in the temperature of reflux for 24 h. After this time, excess of  $\text{K}_2\text{CO}_3$  was filtered off. The solvent from the filtrate was removed under reduced pressure and the residue was purified by column chromatography (chloroform). After chromatography, the product was dissolved in a minimal amount of chloroform and precipitated with hexanes. Precipitate was filtered off and dried to afford white solid **1CM**. Yield was equal to 56% (0.28 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.29 (d,  $J = 2.0$  Hz, 1H, ArH), 8.04 (d,  $J = 7.5$  Hz, 1H, ArH), 7.70–7.55 (m, 2H, ArH), 7.51–7.43 (m, 1H, ArH), 7.42–7.32 (m, 2H, ArH), 7.21 (t,  $J = 7.3$  Hz, 1H, ArH), 4.27 (t,  $J = 7.2$  Hz, 2H,  $\text{N}-\text{CH}_2-$ ), 4.00 (s, 6H,  $\text{OCH}_3$ ), 1.85 (q,  $J = 7.2$  Hz, 2H,  $\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.47–1.09 (m, 10H, CH aliphatic), 0.86 (t,  $J = 6.7$  Hz, 3H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.09, 141.19, 138.01, 129.49, 126.07, 123.11, 122.83, 120.94, 120.56, 118.92, 114.14, 109.05, 108.87, 54.95, 43.41, 31.98, 29.56, 29.36, 29.20, 27.51, 22.79, 14.24. ESI-MS  $m/z$  calc for  $\text{C}_{25}\text{H}_{31}\text{N}_5\text{O}_2$ , 433.25; found 434.4. M.p.: 116–117 °C, 121 °C (DSC)

#### 6-Methoxy-N<sup>2</sup>,N<sup>4</sup>-bis(9-octyl-9H-carbazol-3-yl)-1,3,5-triazine-2,4-diamine (2CM)

A solution of 2,4-dichloro-6-methoxy-1,3,5-triazine (0.13 g, 0.72 mmol), 9-octyl-9H-carbazol-3-amine (0.42 g, 1.44 mmol) and  $\text{K}_2\text{CO}_3$  (0.2 g, 1.44 mmol) in 25 ml of THF was heated in the temperature of reflux for 24 h. After this time, excess of  $\text{K}_2\text{CO}_3$  was filtered off. Solvent from the filtrate was removed under reduced pressure and the residue was purified by column chromatography (chloroform: ethyl acetate 95:5, v/v). After chromatography, the product was dissolved in a minimal amount of chloroform and precipitated with hexanes. Precipitate was filtered off and dried to afford white solid **2CM**. Yield was equal to 50% (0.25 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.29 (s, 2H), 8.09–7.62 (m, 2H), 7.58 (d,  $J = 8.8$  Hz, 2H), 7.52–7.32 (m, 6H), 7.28–6.79 (m, 4H), 4.22 (s, 4H), 4.01 (s, 3H), 1.81 (s, 4H), 1.51–1.01 (m, 20H), 0.85 (t,  $J = 6.6$  Hz, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.21, 141.19, 137.80, 130.19, 125.93, 123.13, 122.92, 120.91, 120.74, 118.77, 114.00, 108.86, 54.51, 43.43, 32.05, 29.62, 29.44, 29.24, 27.56, 22.86, 14.32. ESI-MS  $m/z$  calc for  $\text{C}_{44}\text{H}_{53}\text{N}_7\text{O}$ , 695.43; found 696.9. M.p.: 140 °C, 139 °C (DSC)

#### N<sup>2</sup>,N<sup>4</sup>,N<sup>6</sup>-tris(9-octyl-9H-carbazol-3-yl)-1,3,5-triazine-2,4,6-triamine (3CM)

A solution of 9-octyl-9H-carbazol-3-amine (0.46 g, 1.56 mmol) and  $\text{K}_2\text{CO}_3$  (0.22 g, 1.56 mmol) in 20 ml of THF was placed on ice bath and stirred for 10 min. After this time, a solution cyanuric chloride (0.096 g, 0.52 mmol) in 10 ml THF was added dropwise over ten minutes. Reaction was carried for 2 h in the temperature of 0 °C and then in reflux for 24 h. Afterwards, excess of  $\text{K}_2\text{CO}_3$  was filtered off, solvent from the filtrate was removed under reduced pressure and the residue was purified by column chromatography (chloroform: ethyl acetate 90:10, v/v). After chromatography, the product was dissolved in a minimal amount of chloroform and precipitated with hexanes. Precipitate was filtered off and dried to afford white solid **3CM**. Yield was equal to 74% (0.37 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (s, 3H, ArH), 8.04–7.49 (m, 9H, ArH), 7.46–7.29 (m, 6H, ArH), 7.27–6.79 (m, 6H, ArH), 4.14 (t,  $J = 6.8$  Hz, 6H,  $\text{N}-\text{CH}_2-$ ), 1.74 (brs, 6H,  $\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.43–1.06 (m, 30H, CH aliphatic), 0.85 (t,  $J = 6.8$  Hz, 9H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$

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