



## Derivatives of 2-phenylindole and carbazole as host materials for phosphorescent organic light emitting diodes



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### ARTICLE INFO

#### Article history:

Received 27 June 2016

Received in revised form

13 September 2016

Accepted 15 September 2016

Available online 29 September 2016

#### Keywords:

Indoleo

Carbazoleo

Phosphorescenceo

PHOLEDs

### ABSTRACT

Synthesis and thermal, electrochemical, photophysical and charge-transporting properties of the derivatives of carbazole and 2-phenylindole are reported. Compounds with reactive functional groups are emphasized. Two compounds form molecular glasses with the glass transition temperatures of 57 °C and 134 °C. The synthesized compounds absorb electromagnetic radiation in the range of 200–375 nm and emit in the range of 350–550 nm. Their solutions exhibit Stokes shifts up to 81 nm. Their triplet energy levels were found to be in the range of 2.88–3.04 eV. The ionization potentials of the synthesized compounds were found to range from 5.45 eV to 5.88 eV. The ability of photopolymerization in the solid state of the synthesized monomers was demonstrated by ATR-FTIR spectroscopy. The charge transporting properties were studied by the space-charge-limited current (SCLC) method. The zero-field hole mobilities reaching  $1.97 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were observed. According to the results of characterization, two compounds were selected for studying them as the hosts in blue and green phosphorescent organic light emitting diodes. The best fabricated device consisting of indium tin oxide anode, hole-transporting layer, emitting layer with 3-((1-(4-vinylbenzyl)-2-phenyl-1*H*-indol-3-yl)methyl)-9-ethyl-9*H*-carbazole as a host and the green emitter, electron transporting layer and calcium layer topped with aluminum layer as cathode, exhibited the maximum current, power, and external quantum efficiencies of 10.3 cd/A, 7.2 lm/W, 2.9%, respectively, in the absence of light out-coupling enhancement. The devices based on the twin derivatives of 2-phenylindolylcarbazolylmethane demonstrated the relatively low values of the turn-on voltages of 3.7 and 3.1 V as well as the efficiency roll-offs of 12.5 and 22.7%.

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## 1. Introduction

Phosphorescent organic light emitting diodes (OLEDs) are a prime focus of organic light emitting device research due to their high light-emitting efficiency efficiencies [1]. The efficiencies of light emission from fluorescent OLEDs are limited compared to that from OLEDs with phosphorescent (triplet) emitters. In a device without triplet emitters only the singlet excitons can be as high as 100% since the triplet emitters can harvest both singlet and triplet excitons [2]. The selection of high-triplet-energy host materials is of great importance for the preparation of efficient phosphorescent OLEDs [3]. Effective charge transport, good thermal stability, high

triplet energy, capability of glass formation are the reasons why electron-rich carbazole moieties are widely used in the design of electroactive compounds [4,5]. Derivatives of carbazole with electronically isolated electroactive groups exhibit high triplet energies [6]. They showed good performance as host materials of blue phosphorescent OLEDs [7,8]. Derivatives of indole were also reported to exhibit high triplet energies [9]. However, their applicability in phosphorescent OLEDs is much less explored.

The strategy of this work was to combine carbazole and indole moieties in the design and synthesis of host materials for phosphorescent OLEDs exhibiting high triplet energy values, charge-transporting and glass-forming abilities. A series of new derivatives of 2-phenylindole and carbazole were synthesized and studied. The materials with the most suitable sets of the properties were tested as host materials in green phosphorescent light emitting diodes.

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## 2. Experimental

### 2.1. Materials

2-Phenylindole-3-carbaldehyde, 2-phenylindole, potassium *tert*-butoxide, iron (III) chloride, zinc, titanium tetrachloride, sodium carbonate, tetrabutylammonium hexafluorophosphate, benzyltrimethylammonium chloride (BTMAC), 4-vinylbenzylchloride, bromoethane, epichlorohydrin, 9-ethylcarbazole, cyclopentadienyl(fluorene)iron(II)hexafluorophosphate, boron trifluoride diethyl etherate (all from Aldrich), 9H-carbazole (Reakhim) were used as received. 3-Hydroxymethyl-2-phenylindole (**HMPI**) was synthesized as described before [10].

3-((9H-Carbazol-3-yl)(2-phenyl-1H-indol-3-yl)methyl)-9H-carbazole (**CPIC**). To a mixture of 9H-carbazole (5 g, 30 mmol) and 2-phenylindole-3-carbaldehyde (3.3 g, 15 mmol) in chloroform (40 ml), hydrochloric acid (conc., 5 ml) was added dropwise and the reaction mixture was stirred at room temperature for 8 h. Then, water (10 ml) was added to quench the reaction and the mixture was stirred vigorously for the additional 10 min. The crude product was extracted with chloroform several times. The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane:ethylacetate (1:6) as an eluent. Yield of reddish powder was 4.5 g (56%).  $M_w = 537$  g/mol.  $C_{39}H_{27}N_3$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.34 (s, 3H, NH), 8.23–7.72 (m, 9H, Ar.), 7.60–7.48 (m, 14H, Ar.), 5.41 (s, 1H, Ar–CH).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  139, 126, 124, 119, 50.

Bis(2-phenyl-1H-indol-3-yl)methane (**BPIM**). To a mechanically stirred solution of 3-hydroxymethyl-2-phenylindole (1.3 g 5.8 mmol) and 2-phenylindole (1.12 g, 5.8 mmol) in dry dichloromethane (40 ml), boron trifluoride diethyl etherate (3.2 ml) was added dropwise and the reaction mixture was stirred at room temperature for 3 h. The crude product was extracted with dichloromethane several times. The dichloromethane solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane:ethylacetate (1:9) as an eluent. Yield of greenish powder was 1.1 g (62%).  $M_w = 398$  g/mol.  $C_{29}H_{22}N_2$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.33 (s, 2H, NH), 8.00–7.74 (m, 18H, Ar.), 5.41 (s, 2H, Ar–CH).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  141, 137, 129, 127, 126, 123, 121, 119, 22.

3-((2-Phenyl-1H-indol-3-yl)methyl)-9H-carbazole (**PIMC**). To a mechanically stirred solution of 3-hydroxymethyl-2-phenylindole (1.3 g 5.8 mmol) and 9-ethylcarbazole (1.5 g, 5.8 mmol) in dry dichloromethane (40 ml), boron trifluoride diethyl etherate (3.2 ml) was added dropwise and the reaction mixture was stirred at room temperature for 3 h. The crude product was extracted with dichloromethane several times. The dichloromethane solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane:ethylacetate (1:9) as an eluent. Yield of greenish powder was 1.3 g (58%).  $M_w = 400$  g/mol.  $C_{29}H_{24}N_2$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  10.01 (s, 1H, NH), 8.00–7.74 (m, 9H), 7.43–7.15 (m, 7H), 5.69 (s, 2H, Ar–CH), 4.04 (q, 2H,  $J = 7.1$  Hz,  $CH_2$ ), 1.32 (t, 3H,  $J = 7.1$  Hz,  $CH_3$ ).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  141, 137, 133, 128, 121, 118, 112, 111, 108, 37, 30, 14.

9-(4-Vinylbenzyl)-3-((1-(4-vinylbenzyl))-2-phenyl-indol-3-yl)(9-(4-vinylbenzyl)-carbazol-3-yl)methyl)-carbazole (**1**) was prepared by the procedure similar to that described elsewhere [11]. To a mechanically stirred mixture of 3-((9H-carbazol-3-yl)(2-phenyl-1H-indol-3-yl)methyl)-9H-carbazole (**CPIC**) (0.7 g, 1.3 mmol), dimethyl sulphoxide (DMSO) (10 ml), potassium *tert*-butoxide (0.04 g, 0.4 mmol), BTMAC (0.04 g, 0.01 mmol) and 4-vinylbenzylchloride (1 ml, 7.8 mmol) were added. The resulting

mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (8 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml  $\times$  3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent. Yield of reddish powder was 0.86 g (75%).  $M_w = 886$  g/mol.  $C_{66}H_{51}N_3$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.23–7.72 (m, 9H, Ar.), 7.60–7.48 (m, 14H, Ar.), 7.21–7.07 (m, 12H), 6.62 (m, 3H, AMX system  $CH=CH_2$  proton  $H^A$ ), 5.67 (dd, 3H, AMX system  $-CH=CH_2$  proton  $H^M$  trans  $J_{AM} = 5.75$  Hz and gem  $J_{MX} = 5.80$  Hz), 5.41 (s, 1H, Ar–CH), 5.18 (d, 3H, AMX system of  $-CH=CH_2$  proton  $H^X$  cis  $J_{AX} = 11$  Hz), 3.39 (s, 6H,  $CH_2$ ).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  139, 125, 123, 119, 110, 50, 45. FT-IR (KBr)  $cm^{-1}$ : 3050 ( $\nu$  C–H Ar), 2919 ( $\nu$  C–H aliph.), 1450 ( $\nu$  C=C Ar), 1363 ( $\nu$  C–N Ar), 995, 928 (C–H of vinyl group), 841, 820, 745 ( $\gamma$  C–H Ar). Elemental analysis for  $C_{66}H_{51}N_3$ . % Calc.: C, 89.46; H, 5.80; N, 4.74; % Found: C, 89.41; H, 5.85; N, 4.69. MS:  $m/z$  886 [ $M^+$ ].

9-((Oxiran-2-yl)methyl)-3-((1-(oxiran-2-yl)methyl)-2-phenyl-indol-3-yl)(9-((oxiran-2-yl)methyl)-carbazol-3-yl)methyl)-carbazole (**2**). A solution of 3-((9H-carbazol-3-yl)(2-phenyl-1H-indol-3-yl)methyl)-9H-carbazole (**CPIC**) (0.7 g, 1.3 mmol) potassium in epichlorohydrin (4 ml, 51 mmol) was stirred at 120 °C for 24 h under argon atmosphere. Then epichlorohydrin was removed by distillation. The product was purified by silica gel column chromatography using hexane as an eluent. It was recrystallized from methanol. Yield of reddish crystals was 0.74 g (81%). M.p. 110 °C (DSC).  $M_w = 705$  g/mol.  $C_{48}H_{39}N_3O_3$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.88 (d, 9H,  $J = 7.8$  Hz, Ar.), 7.28–7.22 (m, 7H, Ar.), 7.1–7.0 (m, 7H, Ar.), 5.07 (s, 1H, Ar–CH), 4.40 (dd, 6H,  $J = 15.8$ ,  $J = 3.4$  Hz,  $CH_2$ ), 4.18 (dd, 4H,  $J = 15.8$ ,  $J = 8.1$  Hz,  $CH_2$ ), 3.12 (d, 2H,  $J = 6.4$  Hz,  $CH_2$ ), 2.57 (t, 3H,  $J = 4.1$  Hz, CH).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  140, 125, 123, 119, 109, 50, 45. FT-IR (KBr)  $cm^{-1}$ : 3052 ( $\nu$  C–H Ar), 2920 ( $\nu$  C–H aliph.), 1453 ( $\nu$  C=C Ar), 1351 ( $\nu$  C–N Ar), 1220 ( $\nu$  C–O–C), 841, 779 ( $\gamma$  C–H Ar). Elemental analysis for  $C_{48}H_{39}N_3O_3$ . % Calc.: C, 81.68; H, 5.57; N, 5.95; O, 6.80; % Found: C, 81.63; H, 5.52; N, 5.90; O, 6.85. MS:  $m/z$  706 [ $(M+H)^+$ ].

9-Ethyl-3-((1-ethyl-2-phenyl-1H-indol-3-yl)(9-ethyl-9H-carbazol-3-yl)methyl)-9H-carbazole (**3**). To a mechanically stirred mixture of 3-((9H-carbazol-3-yl)(2-phenyl-1H-indol-3-yl)methyl)-9H-carbazole (**CPIC**) (0.7 g, 1.3 mmol), dimethylsulfoxide (10 ml), potassium *tert*-butoxide (0.44 g, 3.9 mmol), BTMAC (0.04 g, 0.01 mmol) and bromoethane (0.58 ml, 7.8 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (8 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml  $\times$  3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent. Yield of reddish powder was 0.53 g (66%).  $M_w = 621$  g/mol.  $C_{45}H_{39}N_3$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.89 (d, 9H,  $J = 7.8$  Hz, Ar.), 7.38–7.29 (m, 7H, Ar.), 7.2–7.11 (m, 7H, Ar.), 5.20 (s, 1H, Ar–CH), 4.02 (q, 6H,  $J = 7.3$  Hz,  $CH_2$ ), 1.32 (t, 9H,  $J = 7.1$  Hz,  $CH_3$ ).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  139, 125, 123, 119, 110, 50, 45. FT-IR (KBr)  $cm^{-1}$ : 3052 ( $\nu$  C–H Ar), 2925 ( $\nu$  C–H aliph.), 1492, 1450 ( $\nu$  C=C Ar), 1358 ( $\nu$  C–N Ar), 842, 745 ( $\gamma$  C–H Ar). Elemental analysis for  $C_{45}H_{39}N_3$ . % Calc.: C, 86.92; H, 6.32; N, 6.76; % Found: C, 86.87; H, 6.37; N, 6.71. MS:  $m/z$  635 [ $(M+Na)^+$ ].

1-(4-Vinylbenzyl)-3-((1-(4-vinylbenzyl))-3,7-dihydro-2-phenyl-1H-indol-3-yl)methyl)-2-phenyl-1H-indole (**4**). To a mechanically stirred solution of bis(2-phenyl-1H-indol-3-yl)methane (**BPIM**) (1.5 g, 3.7 mmol) in dimethylsulfoxide (10 ml), potassium *tert*-butoxide (1.26 g, 11.3 mmol), BTMAC (0.04 g, 0.01 mmol) and 4-vinylbenzylchloride (2.1 ml, 15.6 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (8 ml)

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