

# Indolyl-substituted carbazole derivatives as amorphous electro-active materials for optoelectronics

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## Abstract

Various indolyl-substituted carbazole derivatives were synthesized and found to constitute glass-forming materials with glass transition temperatures in the range of 40–95 °C as characterised by differential scanning calorimetry. The electron photoemission spectra of the materials were recorded and the ionisation potentials of 5.2–5.7 eV were established. Time-of-flight hole drift mobility of the indolyl-substituted carbazole dihydrazone molecularly dispersed in bisphenol Z polycarbonate approached  $4 \times 10^{-6} \text{ cm}^2/\text{V s}$  at high electric field.

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## 1. Introduction

Low molecular weight organic compounds that readily form stable glasses are called molecular glasses or amorphous molecular materials. They show excellent processability, transparency, isotropic and homogeneous properties and receive growing attention both in terms of academic interest and technological applications. Aromatic amine and/or hydrazone based molecular glasses belong to the classes of light emitting and charge-transporting materials and are known for various applications such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells, photorefractive materials [1,2].

For the purpose of developing electronically active molecular glasses, we have been studying the synthesis, properties and applications of novel molecules based on aromatic amines, hydrazones and other classes of organic compounds. We have reported previously several series of hole-transporting compounds: 3,6-di(aryl)carbazoles having different substituents at 9th position of the central carbazole ring [3,4] as well as carbazole-based dihydrazones [5,6]. The carbazole derivatives showed hole drift mobilities up to  $10^{-2} \text{ cm}^2/\text{V s}$  at high electric fields [5].

In the present study we report on the synthesis and properties of glass-forming indolyl-containing compounds. Indolyl group until now is a relatively little studied as a building block in the design and synthesis of organic electro-active materials.

## 2. Experimental

### 2.1. Instrumentation

<sup>1</sup>H NMR spectra were recorded using Varian Unity Inova and JOEL JNM-FX 100 apparatuses. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using Perkin-Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys™ 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer Pyris Diamond calorimeter. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [7,8]. The samples for the ionisation potential measurement were prepared as described previously [3].

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The hole drift mobility was measured by the xerographic time of flight technique in [9]. The samples for the charge carrier mobility measurements were prepared by casting the mixtures in weight proportion 1:1 with polycarbonate Z (PC-Z) on polyester films with Al layer. The thickness of the charge transport layer varied in the range of 3–10  $\mu\text{m}$ .

## 2.2. Materials

9H-Carbazole (**1**), indole (**5**) and *N*-methyl-*N*-phenylhydrazine (**9**) were purchased from Aldrich and used as received.

3,6-Diiodo-9H-carbazole (**2**) was obtained by a modified procedure of Tucker [10]. 3,6-Diiodo-9-alkylcarbazoles (**3** and **4**) were prepared by alkylation of 3,6-diiodo-9H-carbazole (**2**) in the presence of a phase transfer catalyst [11].

### 2.2.1. 3,6-Di(indol-1-yl)-9-butylcarbazole (**6**)

4.13 g (35.22 mmol) of indole, 5.6 g (11.74 mmol) of 3,6-diiodo-9-butylcarbazole, powdered potassium carbonate (13 g, 93.92 mmol), copper powder (2.98 g, 46.96 mmol) and 18-crown-6 (0.62 g, 2.35 mmol) were refluxed in *o*-dichlorobenzene (20 ml) under nitrogen for 24 h. Copper powder and inorganic salts were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by silica gel column using hexane/acetone (vol. ratio 20:1) as an eluent. Compound **6** was crystallized from the eluent to yield 0.5 g of grey crystals (mp: 143 °C). IR  $\nu_{\text{max}}$  (KBr): 3050 ( $\text{CH}_{\text{ar}}$ ), 2952, 2925, 2868 ( $\text{CH}_{\text{aliphatic}}$ ), 1610, 1495, 1482, 1458 ( $\text{C}=\text{C}_{\text{ar}}$ ). MS (eV):  $m/z = 454$  ( $M^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.09 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.0$ ), 1.49–1.62 (m, 2H,  $-\text{CH}_2-$ ), 1.97–2.07 (m, 2H,  $-\text{CH}_2-$ ), 4.47 (t, 2H,  $-\text{CH}_2-\text{N}-$ ,  $J = 7.0$ ), 6.78–8.22 (m, 18H,  $-\text{CH}_{\text{ar}}$ ).

### 2.2.2. 3,6-Di(indol-1-yl)-9-(2-ethylhexyl)carbazole (**7**)

3.7 g (31.7 mmol) of indole, 4.21 g (7.93 mmol) of 3,6-diiodo-9-(2-ethylhexyl)carbazole, powdered potassium carbonate (13.7 g, 99.06 mmol), copper powder (3.12 g, 49.14 mmol) and 18-crown-6 (0.42 g, 1.6 mmol) were refluxed in 20 ml of *o*-dichlorobenzene under nitrogen for 24 h. Inorganic salts were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by silica gel column using hexane/acetone (vol. ratio 25:1) as an eluent. The compound **7** was crystallized from the eluent to yield 4 g of white crystals (mp: 162 °C). IR  $\nu_{\text{max}}$  (KBr): 3046 ( $\text{CH}_{\text{ar}}$ ), 2957, 2930, 2856 ( $\text{CH}_{\text{aliphatic}}$ ), 1608, 1493, 1458 ( $\text{C}=\text{C}_{\text{ar}}$ ). MS (eV):  $m/z = 510$  ( $M^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.0 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.0$ ), 1.08 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.3$ ), 1.34–1.60 (m, 8H,  $-\text{CH}_2-$ ), 2.22–2.28 (m, 1H,  $-\text{CH}-$ ), 4.35 (d, 2H,  $-\text{CH}_2-\text{N}-$ ,  $J = 9.0$ ), 6.79–8.23 (m, 18H,  $\text{CH}_{\text{ar}}$ ).

3,6-Di[(3-formyl)indol-1-yl]-9-(2-ethylhexyl)carbazole (**8**) was synthesized by Vilsmeier reaction [12] of 3,6-di(indol-1-yl)-9-(2-ethylhexyl)carbazole by the following procedure.  $\text{POCl}_3$  was added dropwise to dry DMF (molar ratio 1:1.2) at 0 °C under nitrogen atmosphere. 4.3 g (123 mmol) of 3,6-di(indol-1-

yl)-9-(2-ethylhexyl)carbazole was dissolved in 7 g (148 mmol) of DMF and the solution was added stepwise to the reaction flask. The reaction mixture was stirred at 85 °C until the starting compound was reacted. Then the reaction mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH 6–8. The precipitated product was filtered and dried. Yield: 4 g of yellow powder. IR  $\nu_{\text{max}}$  (KBr): 3046 ( $\text{CH}_{\text{ar}}$ ), 2957, 2928, 2858 ( $\text{CH}_{\text{aliphatic}}$ ), 1652 (CHO), 1497, 1462, 1421 ( $\text{C}=\text{C}_{\text{ar}}$ ). MS (eV):  $m/z = 566$  ( $M^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.84 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.0$ ), 0.92 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.0$ ), 1.18–1.46 (m, 6H,  $-\text{CH}_2-$ ), 2.07–2.15 (m, 1H,  $-\text{CH}-$ ), 3.77 (d, 2H,  $-\text{CH}_2(\text{H-6})$ ,  $J = 3$ ), 4.44–4.53 (m, 2H,  $-\text{CH}_2-\text{N}-$ ), 7.34–8.85 (m, 16H,  $-\text{CH}_{\text{ar}}$ ), 10.1 (s, 2H,  $-\text{CHO}$ ).

### 2.2.3. 3,6-Di(3-(*N*-methyl-*N*-phenylamino)iminomethyl)indol-1-yl)-9-(2-ethylhexyl)carbazole (**10**)

Solution of *N*-methyl-*N*-phenylhydrazine (0.9 g, 21.2 mmol) in methanol was added dropwise to methanol solution of 3,6-di[(3-formyl)indol-1-yl]-9-(2-ethylhexyl)carbazole (1 g, 5.3 mmol) by stirring. The reaction mixture was refluxed for 20 min, until all carbaldehyde was reacted (TLC control). Then the reaction mixture was cooled down to the room temperature. The precipitated product was filtered and dried. Yield: 0.7 g of yellow powder. IR  $\nu_{\text{max}}$  (KBr): 3049 ( $\text{CH}_{\text{ar}}$ ), 2956, 2927, 2871 ( $\text{CH}_{\text{aliphatic}}$ ), 1597 ( $\text{C}=\text{N}$ ), 1495, 1457 ( $\text{C}=\text{C}_{\text{ar}}$ ), 1310 ( $\text{C}-\text{N}$ ). MS (eV):  $m/z = 774$  ( $M^+$ ).  $^1\text{H}$  NMR (300 MHz, DMSO),  $\delta$  (ppm): 0.83 (t, 3H,  $-\text{CH}_3$ ,  $J = 6.6$ ), 0.92 (t, 3H,  $-\text{CH}_3$ ,  $J = 7.3$ ), 1.19–1.45 (m, 8H,  $-\text{CH}_2-$ ), 2.05–2.13 (m, 1H,  $-\text{CH}-$ ), 3.43 (s, 6H,  $-\text{CH}_3$ ), 4.37 (d, 2H,  $-\text{CH}_2-$ ,  $J = 6.6$ ), 6.85–8.48 (m, 26H,  $-\text{CH}_{\text{ar}}$ ), 8.6 (s, 2H,  $-\text{CH}$ ).

## 3. Results and discussion

3,6-Di(indol-1-yl)-9-alkylcarbazoles (**6** and **7**) were prepared as described in Scheme 1 via the Ullmann coupling reaction of the corresponding 3,6-diiodo-9-alkylcarbazole (**3** or **4**) with an excess of indole (**5**). The diiodo-derivatives (**3–4**) were prepared by alkylation of 3,6-diiodo-9H-carbazole (**2**) which was synthesized by the Tucker iodination of 9H-carbazole (**1**) in the presence of KI and  $\text{KIO}_3$ .

3,6-Di(indol-1-yl)-9-(2-ethylhexyl)carbazole (**7**) was used for the preparation of dihydrazone **10** by two-step reaction as shown in Scheme 1. The first step was Vilsmeier formylation of the indolyl groups to get diformyl derivative **8**. The second step was condensation of the dialdehyde with *N*-methyl-*N*-phenylhydrazine (**9**).

All the newly synthesized compounds were identified by mass spectrometry, IR and electronic absorption, as well as  $^1\text{H}$  NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The indolyl substituted carbazole derivatives (**6**, **7** and **10**) were readily soluble in common organic solvents, such as tetrachloroethane, chloroform, THF and acetone at the room temperature. Transparent thin amorphous films of these materials could be prepared by casting or spin coating from solutions.

Thermal properties of the synthesized materials were examined using DSC and TGA analysis under a nitrogen atmosphere.

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