

# Synthesis and properties of glass-forming condensed aromatic amines with reactive functional groups

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## Abstract

A series of new glass-forming condensed aromatic amines containing functional groups was synthesized by stepwise route and characterized by nuclear magnetic resonance, infrared and mass spectrometry. The thermal, optical and photoelectrical properties of the synthesized compounds are reported. The synthesized aromatic amines form glasses with the glass transition temperatures in the range of 73–104 °C as characterized by differential scanning calorimetry. The ionisation potentials of these compounds range from 5.25 to 5.36 eV as determined by electron photoemission method. The best charge transport properties were shown by di(4-(4-(3,6-di(*N,N*-diphenylamino)carbazole-9)-phenoxy-2-hydroxypropylthio)phenyl)sulphide. Room temperature hole-drift mobilities in its 50% solid solutions in bisphenol Z polycarbonate established by the xerographic time-of-flight technique were found to be  $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at electric field of  $6.4 \times 10^5 \text{ V cm}^{-1}$ .

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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 process ability, transparency, isotropic and homogeneous properties and receive growing attention both in terms of academic interest and technological applications. Aromatic amine-based molecular glasses belong to the class of hole-transporting materials which are known for various applications such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells and photorefractive materials [1–3]. In multi-layer optoelectronic devices cross-linked charge transport or electroluminescent layers are preferable. Using cross-linkable materials upper layers can be prepared on the cross-linked under layer simple by casting or spin coating techniques. In addition, no diffusion between layers occurs when cross-linked materials are used. For the preparation of cross-linked layers organic electroactive materials with reactive functional groups are necessary.

In the present study, we report on the synthesis and investigation of the properties of glass-forming condensed aromatic amines with the functional hydroxyl and epoxy groups.

## 2. Experimental

### 2.1. Materials

The starting compounds: 9*H*-carbazole, diphenylamine, 4-iodoanisole, sodium hydride, ethanethiol, epichlorohydrin, 4,4'-thiobisbenzenethiol were purchased from "Aldrich" and used as received. All the required chemicals: 18-crown-6, potassium carbonate, copper powder, potassium iodide, potassium iodate, benzyltrimethylammonium chloride (BTMA), magnesium sulphate, triethylamine (TEA) were also purchased from "Aldrich". Organic solvents were purified and dried by standard methods [4]. Silica gel was used for column chromatography.

#### 2.1.1. 9-(4-Methoxyphenyl) carbazole (I)

5.51 g (33 mmol) of carbazole, 10 g (43 mmol) of 4-iodoanisole, powdered potassium carbonate (36.43 g, 264 mmol), copper powder (8.38 g, 132 mmol) and 18-crown-6 (0.56 g, 2.1 mmol) were refluxed in 30 ml *o*-dichlorobenzene under nitrogen for 24 h. Then, copper and inorganic salts were filtered off. The solvent was removed by distillation. The product was crystallized from methanol, filtered and dried. Yield: 8.432 g (93.7%) of white crystals (mp: 154.1–155.4 °C). FW = 273 g mol<sup>-1</sup>. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3044, 3016 (CH<sub>ar</sub>),

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2959, 2837 (CH<sub>aliphatic</sub>), 1593, 1514, 1479 (C=C<sub>ar</sub>), 1248 (C—O—C). MS (eV):  $m/z$  = 274 ( $M^+$ ), 242, 166. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 4.04 (s, 3H, methoxy), 7.24–7.63 (m, 8H, —CH<sub>ar</sub>), 8.35–8.40 (m, 4H, —CH<sub>ar</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 55.95, 110.07, 115.44, 120.03, 120.68, 123.53, 126.25, 128.90, 130.65, 141.78, 159.26.

### 2.1.2. 3,6-Diiodo-9-(4-methoxyphenyl)-9H-carbazole (2)

To a stirred mixture of 9-(4-methoxyphenyl)carbazole **1** (9.54 g, 34 mmol), potassium iodide (10.96 g, 66 mmol), acetic acid (150 ml), potassium iodate (16.05 g, 75 mmol) were added at 130 °C and the resulting mixture was stirred and heated for 1 h. After the reaction, most of the acetic acid was removed by rotary evaporation. The inorganic materials were dissolved in water. The organic product was filtered off, washed several times with *iso*-propanol and dried. Yield: 16.07 g (87.6%) of white powder **2**. FW = 525 g mol<sup>-1</sup>. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3055 (CH<sub>ar</sub>), 2995, 2933, 2836 (CH<sub>aliphatic</sub>), 1513, 1465 (C=C<sub>ar</sub>), 1230 (C—O—C). MS (eV):  $m/z$  = 526 ( $M^+$ ), 271, 398, 107. <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 3.94 (s, 3H, methoxy), 6.97–7.67 (m, 6H, —CH<sub>ar</sub>), 8.33–8.42 (m, 4H, —CH<sub>ar</sub>).

### 2.1.3. 3,6-Bis(diphenylamino)-9-(4-methoxyphenyl)carbazole (3)

Six grams (11 mmol) of 3,6-diiodo-9-(4-methoxyphenyl)-9H-carbazole **2**, 3.72 g (22 mmol) of diphenylamine, powdered potassium carbonate (12.14 g, 88 mmol), copper powder (2.79 g, 44 mmol) and 18-crown-6 (0.6 g) were refluxed in 40 ml of *o*-dichlorobenzene under nitrogen for 24 h. Then, copper and inorganic salts were filtered off. The solvent was distilled. The product was crystallized from methanol, filtered and dried. Yield: 6.15 g (89%) of **3** (mp: 144 °C). FW = 607 g mol<sup>-1</sup>. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3035 (CH<sub>ar</sub>), 2932, 2836 (CH<sub>aliphatic</sub>), 1514, 1482 (C=C<sub>ar</sub>), 1225 (C—O—C). MS (eV):  $m/z$  = 608 ( $M^+$ ), 439, 285. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 3.94 (s, 3H, methoxy), 6.95–7.40 (m, 26H, —CH<sub>ar</sub>), 7.42–7.59 (m, 2H, —CH<sub>ar</sub>), 7.90 (s, 2H, —CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 55.52, 110.72, 115.04, 118.69, 121.51, 122.61, 123.67, 125.89, 128.30, 128.98, 138.88, 140.24, 148.46, 154.87.

### 2.1.4. 3,6-Bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole (4)

A solution of sodium ethanethiolate was prepared by adding 4.43 ml (60 mmol) of ethanethiol to a suspension of 0.96 g (40 mmol) of sodium hydride (90%) in 70 ml of dry DMF at 0 °C under N<sub>2</sub>, and then by stirring for 15 min at room temperature. A solution of 2.5 g (4 mmol) of 3,6-bis(diphenylamino)-9-(4-methoxyphenyl)carbazole **3** in 15 ml DMF was added to the former solution and heated at 120 °C for 19 h. The reaction was stopped by carefully adding a few drops of water to the ice cooled solution. A further portion of water (150 ml) was added, followed by acidification with 2N HCl. The precipitated product was filtered off, washed with a large amount of hexane and purified by column chromatography (eluent:hexane/acetone, 3:1). Yield: 2.07 g (84.84%) of **4**. FW = 593 g mol<sup>-1</sup>. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3516 (OH), 3034 (CH<sub>ar</sub>), 1514, 1484 (C=C<sub>ar</sub>). MS (eV):  $m/z$  = 594 ( $M^+$ ), 576, 257. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 5.50 (s, 1H, —OH), 7.00–7.40 (m, 26H, —CH<sub>ar</sub>), 7.42–7.59 (m, 2H, —CH<sub>ar</sub>), 7.90 (s, 2H, —CH<sub>ar</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 110.72, 116.55, 118.69, 121.54, 122.57, 123.67, 125.87, 128.53, 128.98, 138.88, 140.24, 148.46, 154.87.

### 2.1.5.

### 3,6-Bis(diphenylamino)-9-(4-[2,3-epoxypropyl]phenoxy)carbazole (5)

A mixture of 3,6-bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole **4** (5 g, 8.43 mmol), epichlorohydrin (20 ml), BTMA (0.02 g) was heated at reflux for 1 h. Then, the excess of epichlorohydrin was removed at reduced pressure and the oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed several times with water and dried over magnesium sulphate. The solvent was evaporated under vacuum. The precipitated product was filtered off and purified by column chromatography (eluent:toluene/hexane, 4:1). Yield: 3.28 g (60%) of bright green powder **5**. FW = 649 g mol<sup>-1</sup>. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3034 (CH<sub>ar</sub>), 2922, 2853 (CH<sub>aliphatic</sub>), 1513, 1483 (C=C<sub>ar</sub>), 1225 (C—O—C). MS (eV):  $m/z$  = 650 ( $M^+$ ), 481, 313, 149. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.79 (dd, 1H, in oxirane ring), 2.96 (dd, 1H, in oxirane ring), 3.41 (m, 1H, —OCH—), 3.99 (dd, 1H, in —OCH<sub>2</sub>—), 4.35 (dd, 1H, in —OCH<sub>2</sub>—), 6.85–7.47 (m, 30H, aromatic protons). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 44.86, 50.30, 69.33, 110.95, 116.00, 118.92, 121.77, 122.87, 123.97, 126.17, 128.98, 129.27, 139.10, 140.54, 148.76, 158.00.

### 2.1.6. Di(4-(4-(3,6-di(*N,N*-diphenylamino)carbazole-9)-phenoxy-2-hydroxypropylthio)phenyl)sulphide (6)

One gram (1.54 mmol) of compound **5** and 0.19 g (0.77 mmol) of 4,4'-thiobisbenzenethiol were dissolved in 15 ml of ethylmethylketone. The reaction was catalyzed by adding of 0.5 ml of TEA at 80 °C. After 24 h, the reaction was terminated by precipitation into methanol. The precipitated product was filtered off and purified by column chromatography (eluent:hexane/acetone, 3:2). Yield: 1.5 g (63%) of **6**. IR (in KBr),  $\nu$  (cm<sup>-1</sup>): 3426 (OH), 3034 (CH<sub>ar</sub>), 2923, 2867 (CH<sub>aliphatic</sub>), 1512, 1482 (C=C<sub>ar</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 2.71 (m, 2H, —CH), 2.67 (s, 2H, —OH), 3.30 (m, 4H, —SCH<sub>2</sub>), 4.16 (s, 4H, —OCH<sub>2</sub>), 6.85–7.80 (m, 68H, CH<sub>ar</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 37.45, 68.58, 70.40, 110.73, 115.74, 118.74, 121.62, 122.71, 123.80, 125.97, 128.42, 128.48, 129.07, 130.34, 131.60, 133.94, 138.90, 140.42, 148.53, 157.53.

## 2.2. Instrumentation

Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC-821e at 20 °C min<sup>-1</sup> heating rate under N<sub>2</sub> atmosphere. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA 851e at a 20 °C min<sup>-1</sup> heating rate, under nitrogen atmosphere. IR spectra were recorded using Perkin-Elmer FT-IR System. The spectra of solid compounds were performed in a form of KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of deuterated chloroform and deuterated dimethylsulphoxide solutions were obtained on Fovies Trauspim (400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C)), Varian Gemini (300 MHz (<sup>1</sup>H), 75.4 MHz (<sup>13</sup>C)), Varian Unity Inova (300 MHz (<sup>1</sup>H), 75.4 MHz (<sup>13</sup>C)) and JOEL JNM-FX 100 (100 MHz (<sup>1</sup>H)) spectrometers. Electron impact mass spectra were obtained on a Waters 2Q 2000. UV-vis absorption spectra were recorded using Spectronic Genesys<sup>TM</sup> 8 UV/VISIBLE spectrometer. Fluorescence emission and excitation spectra were recorded with Hitachi MPF-4 spectrometer.

The ionisation potentials ( $I_p$ ) of the films of the synthesized compounds were measured by electron photoemission in air method as described before [5,6]. The samples for the measurements were prepared by casting the solutions of the compounds on Al plates pre-coated with methylmethacrylate and methacrylic acid copolymer as adhesive layer.

Hole-drift mobilities were measured by a time-of-flight method in a xerographic regime [7,8]. Positive corona charging created electric field inside the TM layer. Charge carriers were generated at the layer surface by illumination with short UV pulses of xenon flash. The layer surface potential decrease as a result of pulse illumination was up to 3–5% of the initial potential before illumination. The transit time  $t_t$  was determined by the kink on the transient curve in double logarithmic scale. The drift mobility was calculated by the formula  $\mu = d^2/U_0 t_t$ , where  $d$  is the layer thickness and  $U_0$  is the surface potential at the moment of illumination. The samples for the measurements were prepared by casting the solutions of the compounds or solutions of the mixtures of these compounds with polycarbonate Z at mass proportion 1:1 in THF. The substrates were polyester films with Al layer.

## 3. Results and discussion

3,6-Bis(diphenylamino)-9-(4-hydroxyphenyl)carbazole **4** was synthesized by three-step synthetic route as shown in Scheme 1. The first step was the iodination of 9-(4-methoxyphenyl)carbazole **1** using KI and KIO<sub>3</sub>. The second step was an Ullmann coupling of 3,6-diiodo-9-(4-methoxyphenyl)-9H-carbazole **2** with diphenylamine. The final step was demethylation of methoxy group of compound **3** with a solution of sodium ethanethiolate in dimethylformamide at ca. 120 °C. The product was purified by column chromatography.

Di(4-(4-(3,6-di(*N,N*-diphenylamino)carbazole-9)-phenoxy-2-hydroxypropylthio)phenyl)sulphide **6** was synthesized as described in Scheme 2 by two-step procedure involving alkylation of compound **4** with an excess of epichlorohydrin

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