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Carbazolyl-substituted triphenyldiamine derivatives as novel photoconductive amorphous molecular materials

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Abstract

Novel branched molecules, *N*,*N*′-bis(4-carbazol-9-ylphenyl)-*N*,*N*′-diphenyl[1,1′-biphenyl]-4,4′-diamine and *N*,*N*′-bis(4-carbazol-9-ylbiphenyl-4′-yl)-*N*,*N*′-diphenyl[1,1′-biphenyl]-4,4′-diamine, have been synthesised and found to constitute amorphous molecular materials with glass-transition temperatures (T_g) 69 and 107 °C, respectively. The electron photoemission spectra of the amorphous films have been recorded and the ionisation potentials of 5.38–5.46 eV have been established. The hole drift mobility (μ_h) of the carbazolyl-substituted triaryldiamines was studied by the time-of-flight technique and was found to be in the range of 10^{-3} to 10^{-4} cm^2/V s at an applied electric field of 6.4×10^5 V/cm.

Keywords: Amorphous material; Synthesis; Ionisation potential; Hole drift mobility

1. Introduction

Low molar-mass organic compounds that readily form stable glasses receive growing attention both in terms of academic interest and technological applications [1–3]. Some of these materials belong to the classes of light emitting and charge-transporting materials, and are known for various applications such as displays, photovoltaic cells, photorefractive materials and electrophotographic photoreceptors [4–6].

Among the triarylamine derivatives, *N*,*N*,*N*′,*N*′-tetraphenylbenzidine, generally called triphenyldiamine (TPD), is one of the most extensively used as organic hole-transporting (HT) material [7]. It is easily oxidized to form stable radical cation [8,9]. However, TPD and the similar compounds have some drawbacks such as low morphological and thermal stability [10]. We have designed and synthesised novel TPD derivatives having bulky substituents, i.e. carbazol-9-yl or carbazol-9-ylphenyl, which have to enhance the stability of these compounds in an amorphous state and to increase their glass-transition temperatures.

2. Experimental

2.1. Instrumentation

FTIR spectra were measured using a Bio-Rad Digilab FTS-40 spectrometer. ^{1}H NMR spectra were recorded using a Brucker AC 250 (250 MHz) apparatus. UV-Vis spectra were measured with a Hitachi U3000 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 calorimeter. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analysis System 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

Ionisation potentials were established by the electron photoemission technique [11]. The samples for the ionisation potential measurements were prepared and the measurements performed as described previously [12].

The samples for the charge carrier mobility measurements were prepared by casting the solutions of the compounds **5** and **6** or solutions of the mixtures of these compounds with a host polymer polycarbonate-Z (PC-Z) at mass proportion 1:1 in tetrahydrofuran. The substrates were glass plates with conductive SnO_2 layer or polyester film with Al layer. The thickness of the transporting layer varied in the range of 2–10 μm. The hole drift mobility (μ_h) was measured by

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time-of-flight method in electrophotographic regime as described previously [13,14].

2.2. Materials

9H-Carbazole (**1**) was received from Reakhim. 4,4′-Diiodobiphenyl; 1,4-diiodobenzene; *N*,*N*′-diphenylbenzidine (**4**), copper powder, potassium carbonate, 18-crown-6; 1,2-dichlorobenzene were purchased from Aldrich and used as received.

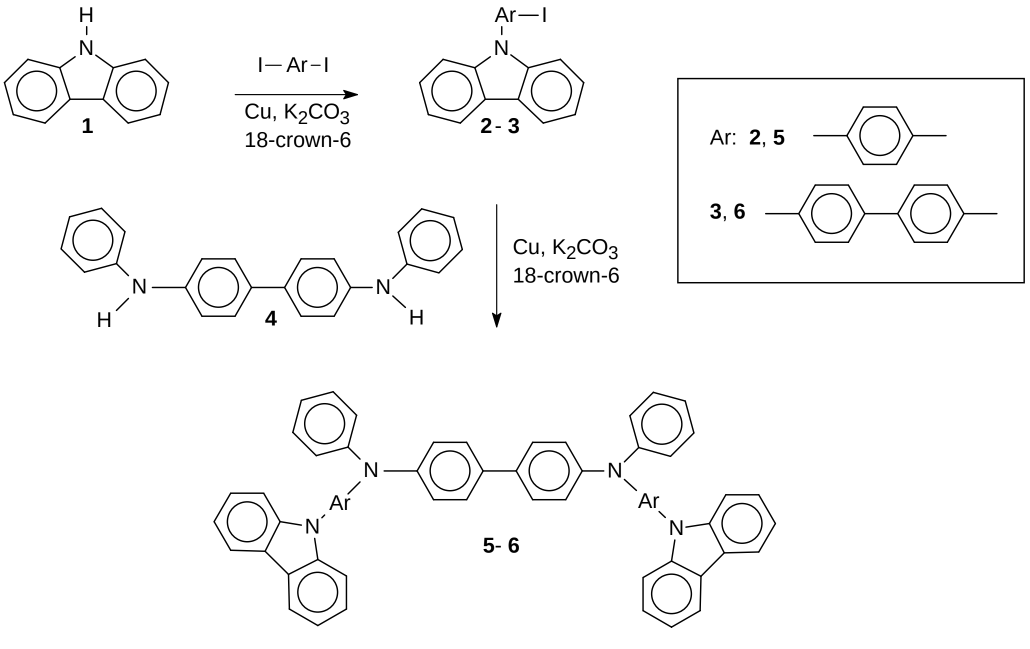
9-(4-Iodophenyl)carbazole (**2**) and 9-[4′-iodo(1,1′-biphenyl)-4-yl]carbazole (**3**) were synthesized by the Ullmann coupling reaction of 1,4-diiodobenzene or 4,4′-diiodobiphenyl, respectively, with an excess of 9H-carbazole (**1**) by a similar procedure as described [15].

N,*N*′-bis(4-Carbazol-9-ylphenyl)-*N*,*N*′-diphenyl[1,1′-biphenyl]-4,4′-diamine (**5**) was synthesized by the Ullmann coupling reaction. Three grams (5.76 mmol) of 9-(4-iodophenyl)carbazole (**2**), 0.7 g (2.06 mmol) of *N*,*N*′-diphenylbenzidine (**4**), 2.27 g (16.45 mmol) of powdered anhydrous potassium carbonate, 0.52 g (8.22 mmol) of copper powder and 0.15 g (0.41 mmol) of 18-crown-6 were refluxed in *o*-dichlorobenzene (20 ml) under nitrogen for 36 h. The copper and inorganic salts were then removed by filtration of the hot reaction mixture, and the product was precipitated into methyl alcohol. The crude product was purified by silica gel column chromatography using hexane/chloroform (volume ratio 4:1) as eluent to obtain **5** as an amorphous substance. Yield: 54%. Elemental analysis for $C_{60}H_{42}N_4$: calc. (%) N 6.85, C 88.02, H 5.13; found (%) N 6.89, C 87.9, H 5.21. MS: $m/z = 819$ (M^+), 750, 716, 708, 641, 599, 563. ^{1}H NMR ($CDCl_3$): δ(ppm) = 7.66 (d, $J = 7.5$, 4H), 7.61–6.82 (m, 38H). FTIR (KBr): $\nu = 3038$, 1604, 1493, 1324, 1280, 1184, 1010, 822, 758, 701 cm^{-1}.

N,*N*′-bis(4-Carbazol-9-ylbiphenyl-4′-yl)-*N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (**6**) was synthesized from 6.1 g (13.37 mmol) of 9-[4′-iodo(1,1′-biphenyl)-4-yl]carbazole (**3**), 1.1 g (3.27 mmol) of *N*,*N*′-diphenylbenzidine, 0.83 g (13.07 mmol) of copper powder, 3.61 g (26.16 mmol) of potassium carbonate and 0.3 g (1.1 mmol) of 18-crown-6 in the analogous way as compound **5**. The crude product was purified by column chromatography using chloroform/hexane (volume ratio 1:4) as eluent. Yield: 54%. Elemental analysis for $C_{72}H_{50}N_4$: calc. (%) N 5.77, C 89.07, H 5.16; found (%) N 5.72, C 89.18, H 5.1; MS: $m/z = 793$, 784, 766, 640, 486 (M^{2+}), 383, 320. ^{1}H NMR ($CDCl_3$): δ(ppm) = 7.75 (d, $J = 8.5$, 2H), 7.6 (d, $J = 7.1$, 4H), 7.58–7.39 (m, 14H), 7.31–7.26 (m, 8H), 7.23–7.14 (m, 18H), 7.11–7.02 (m, 4H). FTIR (KBr): $\nu = 3038$, 1601, 1492, 1324, 1279, 1184, 108, 818, 758, 700 cm^{-1}.

3. Results and discussion

The synthetic route to the carbazolyl-substituted TPD derivatives (**5** and **6**) is shown in Scheme 1. Compounds **5** and **6** were prepared by the Ullmann coupling reaction of *N*,*N*′-diphenylbenzidine (**4**) with an excess of iodo compound, 9-(4-iodophenyl)carbazole (**2**) and 9-[4′-iodo(1,1′-biphenyl)-4-yl]carbazole (**3**), respectively. The key starting iodo compounds (**2** and **3**) were synthesised by the Ullmann reaction of 9H-carbazole (**1**) with an excess of 1,4-diiodobenzene or 4,4′-diiodobiphenyl, respectively. Compounds **2**–**6** were identified by mass spectrometry, IR, ^{1}H NMR spectroscopy and elemental analysis.



Scheme 1.

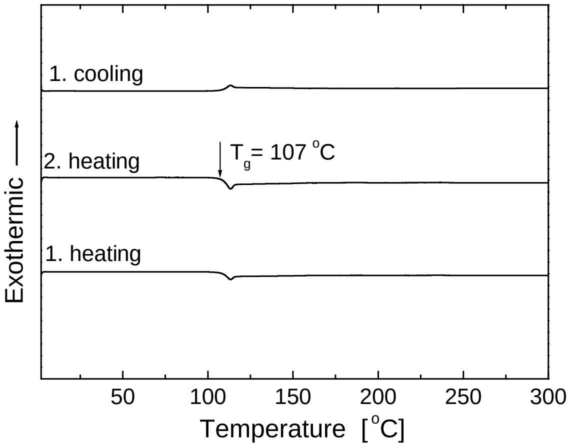


Fig. 1. DSC curves of **6**. Heating rate: 10 °C/min.

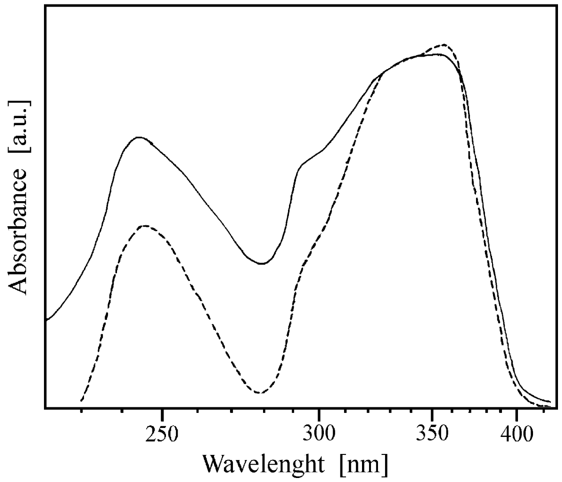


Fig. 2. UV absorption spectra of **5** (solid line) and **6** (dashed line) dilute solutions (10^{-5} mol/l).

The thermal properties of the materials synthesized were examined by DSC and TGA under a nitrogen atmosphere. TGA measurements revealed that the compounds are thermally stable. The onset of decomposition for **5** and **6** occurs only above 300 °C. These compounds were obtained as amorphous glasses as confirmed by DSC. When the samples of **5** and **6** were heated the glass-transition temperatures (T_g) were observed at 69 °C for **5** and at 107 °C for **6**, and no peaks due to crystallisation and melting appeared. Cooling down and the following repeated heating revealed only the glass transition again. As an example, the DSC thermograms of **6** are shown in Fig. 1. The transparent amorphous films of these materials can be prepared by casting or spin coating from solutions.

It is of interest to compare T_g of TPD with that of its carbazolyl-substituted derivatives **5** and **6**. T_g of the TPD glass was reported to be 60 °C [16]. As expected, T_g of the new materials are higher than that of TPD. It is evident that the attachment of bulky carbazol-9-yl group to the TPD core enables not only to increase the stability of glasses but also their T_g. The values of T_g of the compounds can also be varied by incorporation of an additional phenyl group to carbazol-9-yl (cf. T_g of **5** with that of **6**).

The electronic spectra of the new TPD derivatives show bands with absorption maxima (λ_{max}) at 246 and 354 nm for **5**, and at 245 and 359 nm for **6** (Fig. 2). The value of λ_{max} of TPD is 354 nm [17]. This observation indicates that the carbazol-9-yl substituent seems not to make an effect on the conjugation of TPD. Carbazol-9-ylphenyl substituted compound (**6**) because of an extended π-conjugation through the biphenylene unit and the lone electron pair at the nitrogen atom shows small bathochromic shift relative to TPD. In the same manner with the red shift of UV absorbtion, which is interpreted as the extended conjugation, stabilizing the oxidized state of compound **6**, it shows lower value of ionization potential (I_p).

The electron photoemission spectra of the films of compounds **5** and **6** are presented in Fig. 3. The values of I_p are 5.46 eV for **5** and 5.38 eV for **6**. As expected, I_p of the film **6** shows lower value than those of compound **5** and TPD (5.55 eV) [17]. Holes would be injected easily to the layers of the compounds synthesized from the charge generation layer or conductive anode with I_p or work function close to 5.2–5.5 eV. The I_p values for charge generation materials, including those widely used in electrophotographic photoreceptors, such as titanyl phthalocyanines [18,19], perylene pigments [20] and bisazo pigments [21] are in the range of 5.1–5.6 eV.

The I_p values of the reported compounds are higher than that of indium–tin oxide (4.8 eV) which is widely used as an anode in electroluminescent devices [22]. However, the injection barriers of holes from electrode into the layers of **5** and **6** are not very high and could be reduced by using a thin layer of copper phthalocyanine [23]. This observation shows that the oligomers can be used for hole-transport (HT) layers in multilayer electroluminescent devices.

Time-of-flight measurements were used to characterise the charge transport properties of the amorphous films of the

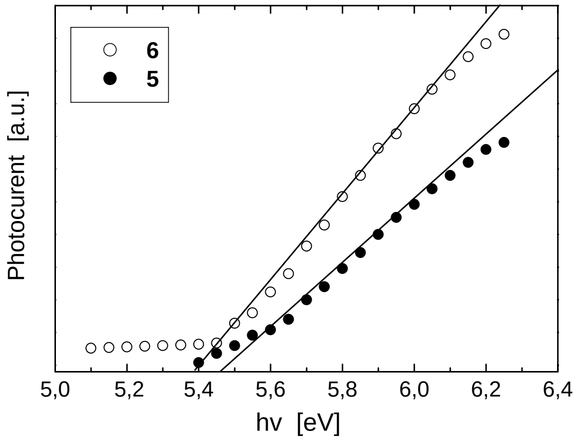


Fig. 3. The electron photoemission spectra of thin films of **5** and **6**.

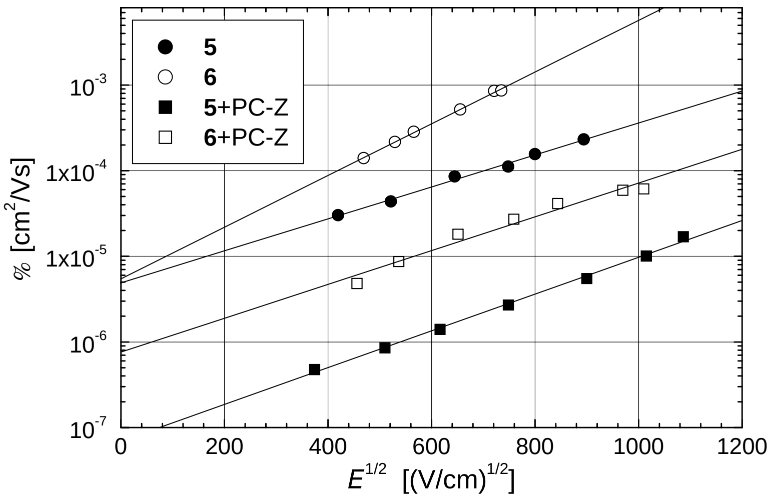


Fig. 4. The electric field dependencies of the hole drift mobility in the amorphous films of compounds **5** and **6**, and their solid solutions in PC-Z.

pure compounds **5** and **6**, and those doped in PC-Z (50 wt.%) (Fig. 4). The room temperature hole drift mobilities (μ_h) of these compounds show linear dependencies on the square root of the electric field. This characteristic dependence is observed for the majority of non-crystalline organic semiconductors and can be attributed to the effects of disorder on charge transport [24].

The μ_h value of 4.7×10^{-4} cm²/V s was observed for the amorphous film of compound **6** at an electric field of 6.4×10^5 V/cm at 293 K. At higher electric fields the positive charge mobilities in this compound approach 10^{-3} cm²/V s. These values are comparable to those reported for TPD which for many years has been known as one of the most effective organic hole-transport materials [25]. Compound **5** shows lower μ_h of ca. 0.5×10^{-4} cm²/V s at an electric field 6.4×10^5 V/cm. The μ_h values of **5** and **6** dispersed in PC-Z are by one and a half order of magnitude lower than those of the neat amorphous films of the compounds. It is understandable since the concentration of the active material in these molecularly doped polymers is only 50%.

In conclusion, we have synthesized the carbazol-9-yl and carbazol-9-ylphenyl substituted *N*,*N*,*N*′,*N*′-tetraphenylbenzidine derivatives which exhibit high thermal stability and form amorphous films with glass-transition temperatures in the range of 69–107 °C. The values of ionisation potential (5.38–5.46 eV) and the hole drift mobility studies show that these compounds can be used as hole-transport materials in electrophotographic photoreceptors and electroluminescent devices.

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