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Triazine-Based Aromatic Amines as New Glass-Forming Charge Transport Materials

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Various diarylamino-substituted 1,3,5-triazine derivatives have been synthesized by Cu catalyzed Ullmann-type arylamino-aryl coupling reaction. Full characterization of the compounds structures by mass spectrometry, IR and electronic absorption, as well as ^1H NMR spectroscopy is presented. Some of the compounds represent amorphous materials with glass transition temperatures exceeding 84°C and with thermal decomposition starting at temperatures $>330^\circ\text{C}$. The electron photoemission spectra of the materials were recorded and the ionisation potentials of ca. 5.3–5.8 eV were established. Time-of-flight hole drift mobility of some diarylamino-substituted triazines molecularly dispersed in bisphenol Z polycarbonate approached $10^{-5}\text{ cm}^2/\text{Vs}$ at high electric field.

Keywords: aromatic amine; glass transition; hole drift mobility; ionisation potential; triazine

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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 and homogeneous properties, and receive growing attention both in terms of academic interest and technological applications. Arylamine and/or triazine based molecular glasses belong to charge-transporting materials and are known for various applications such as electrophotographic photoreceptors, organic light-emitting diodes, photovoltaic cells etc [1–3].

Tris(diphenylamino)-substituted symmetric triazine was discovered more than a century ago [4] and since then several of its chemical behaviours [5,6] and applications to organic light emitting diodes as an electron transport layer [7,8] have been studied. However, most symmetric triazines formed exciplexes or charge transfer complexes between their and the adjacent organic layers, demonstrating that the triazine core has strong electron-accepting characteristics. On the other hand tris(diphenylamino)-substituted symmetric triazine had no clear glass transition temperature (T_g) and its thin films were found to have a polycrystalline morphology [9].

In the present study we report on the synthesis and properties of new unsymmetrical 6-phenyl-1,3,5-triazine core having derivatives substituted with electron rich diarylamino fragments. Tris(ditolylamino)-substituted symmetric triazine was prepared for comparison of their properties. We expected that modifying the triazine electron affinity by introducing electron-donating substitutes will provide compounds with the well-tuned electronic properties required for charge transport in electro-photographic photoreceptors and electroluminescent devices.

2. EXPERIMENTAL

2.1. Instrumentation

^1H 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 GenesysTM 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 [10,11]. The samples for the ionisation potential measurement were prepared as described previously [12].

The charge drift mobility was measured by the xerographic time of flight technique [13]. 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 5–9 μm .

2.2. Materials

9H-Carbazole (**1**), 2,4-diamino-6-phenyl-1,3,5-triazine (**4**), 2,4,6-triamino-1,3,5-triazine (**5**) and 4-iodotoluene (**6**) were purchased from Aldrich and used as received.

3-Iodo-9H-carbazole (**2**) was obtained by a modified procedure of Tucker [14]. 3-Iodo-9-(2-ethylhexyl)carbazole (**3**) was prepared by alkylation of 3-iodo-9H-carbazole (**2**) in the presence of a phase transfer catalyst [15].

2,4-Di{di[9-(2-ethylhexyl)carbazol-3-yl]amino}-6-phenyl-1,3,5-triazine (**7**). 0.19 g (1 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine (**4**), 3.24 g (8 mmol) of 3-iodo-9-(2-ethylhexyl)carbazole (**3**), powdered potassium carbonate (2.2 g, 16 mmol), copper powder (0.51 g, 8 mmol) and 18-crown-6 (0.06 g, 0.24 mmol) were stirred in *o*-dichlorobenzene (10 ml) at 175°C under nitrogen for 30 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 75:1) as an eluent. Yield of the compound **7** was 0.5 g.

IR ν_{max} (KBr): 3052, 2957, 2928, 2858, 1600, 1589, 1537, 1489, 1381. MS (eV): $m/z = 1297([M + 1]^+)$. ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.12–7.89 (m, 6H, CH_{Ar}), 7.52–6.98 (m, 27H, CH_{Ar}), 4.16–3.72 (m, 8H, NCH_2CH), 2.11–1.87 (m, 4H, $\text{NCH}_2\text{CH}(\text{CH}_2)_2$), 1.58–1.12 (m, 32H, $-\text{CH}_2-$), 1.02–0.73 (m, 6H, $-\text{CH}_3$).

2,4-Di{di(4-methylphenyl)amino}-6-phenyl-1,3,5-triazine (**8**). 1 g (5.3 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine (**4**), 5.82 g (26.7 mmol) of 4-iodotoluene (**6**), powdered potassium carbonate (4.5 g, 42.46 mmol), copper powder (1.36 g, 21.4 mmol) and 18-crown-6 (0.3 g, 1.1 mmol) were stirred in *o*-dichlorobenzene (10 ml) at 180°C under nitrogen for 25 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 5:1) as an eluent. Compound **7** was crystallized from the eluent to yield 0.4 g of white crystals (m.p.:152°C).

IR ν_{\max} (KBr): 3060, 3028, 2919, 2860, 1589, 1486, 1447. MS (eV): $m/z = 548([M + 1]^+)$. ^1H NMR (300 MHz, CDCl_3), δ (ppm): 8.16–8.11 (m, 2H, CH_{Ar}), 7.46–7.33 (m, 3H, CH_{Ar}), 7.19 (d, 8H, CH_{Ar} , $J = 8.4$), 7.11 (d, 8H, CH_{Ar} , $J = 8.4$), 2.39 (s, 12H, $-\text{CH}_3$).

2,4,6-Tri[di(4-methylphenyl)amino]-1,3,5-triazine (**9**). 0.3 g (2.3 mmol) of 2,4,6-triamino-1,3,5-triazine (**5**), 6 g (27.7 mmol) of 4-iodotoluene (**6**), powdered potassium carbonate (7.7 g, 55.7 mmol), copper powder (1.75 g, 27.6 mmol) and 18-crown-6 (0.37 g, 1.4 mmol) were stirred in *o*-dichlorobenzene (10 ml) at 175°C under nitrogen for 96 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/THF (vol. ratio 4:1) as an eluent. Compound **7** was crystallized from the eluent to yield 1.3 g of white crystals (m.p.: 267°C).

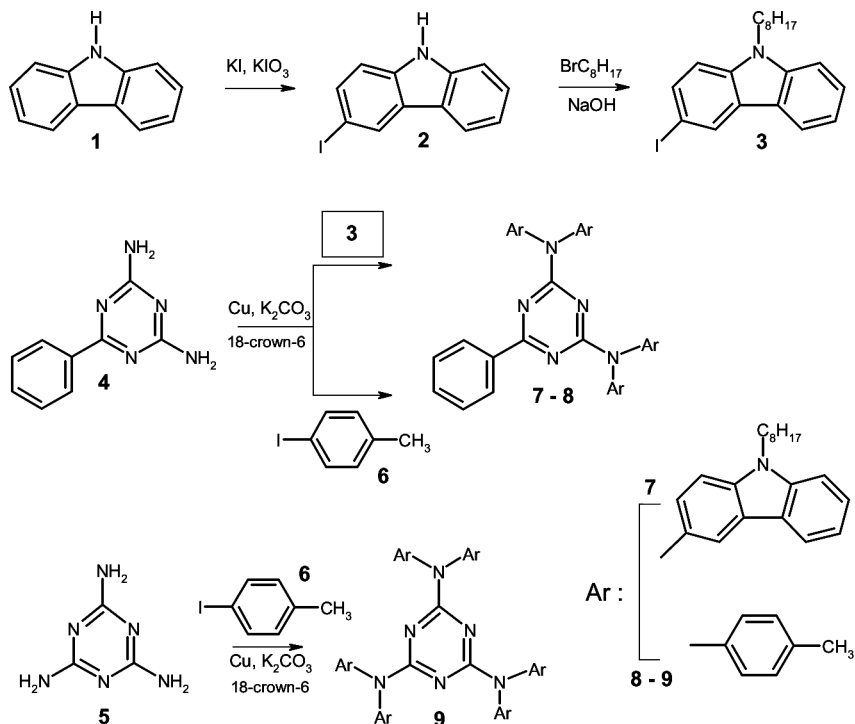
IR ν_{\max} (KBr): 3053, 2958, 2928, 2858, 1589, 1540, 747. MS (eV): $m/z = 667([M + 1]^+)$. ^1H NMR (300 MHz, CDCl_3), δ (ppm): 7.04 (d, 12H, CH_{Ar} , $J = 8.4$), 6.96 (d, 12H, CH_{Ar} , $J = 8.4$), 2.33 (s, 18H, $-\text{CH}_3$).

3. RESULTS AND DISCUSSION

The synthetic route towards the diarylamino substituted 1,3,5-triazines (**7–9**) is shown in Scheme 1. 3-Iodo-9-(2-ethylhexyl)carbazole (**3**) as key starting material was synthesized from 3-iodo-9H-carbazole (**2**) by alkylation with 2-ethylhexylbromide under basic conditions. The iodo-derivative **2** was prepared from commercially available 9H-carbazole (**1**) by Tucker iodination [14] with KI/KIO₃ in acetic acid.

Di(diarylamino)-substituted phenyl-1,3,5-triazines (**7–8**) were synthesized via the modified Ullmann coupling [16] reaction of 2,4-diamino-6-phenyl-1,3,5-triazine (**4**) with an excess of 3-iodo-9-(2-ethylhexyl)carbazole (**3**) or 4-iodotoluene (**6**), respectively. Tris (ditolylamino)-substituted derivative (**9**) was prepared by the Ullmann reaction of melamine (**5**) with an excess of 4-iodotoluene (**6**). All the newly synthesized compounds were identified by mass spectrometry, IR and electronic absorption, as well as ^1H NMR spectroscopy. The data were found to be in good agreement with the proposed structures.

Thermal properties of the synthesized materials were examined using DSC and TGA analysis under a nitrogen atmosphere. TGA measurements revealed that the materials exhibit sufficient thermal stability. The onset of decomposition for the materials was observed at temperatures $>330^\circ\text{C}$. Especially high thermal stability was



SCHEME 1 Synthesis of materials under study.

observed for compound **7**. The temperature of 5% weight loss was detected at ca. 465°C.

The derivative **7** having long alkyl chains was obtained as amorphous material as confirmed by DSC in the temperature range of 0–300°C. During the heating cycles the glass-transitions of the material were observed at 85°C, and no peaks due to crystallization or melting appeared. Repeated thermal cycling of the samples (several cooling and heating cycles) revealed only the glass transition. The ditolylamino substituted triazines (**8–9**) both were obtained as polycrystals by recrystallization from solution. However the derivative **8** formed a glass when its melt sample was cooled. The DSC thermograms of **8** are shown in Figure 1. When the crystalline sample was heated, the endothermic peak due to melting was observed. The melted substance formed a glass upon cooling, i.e., no crystallization peak was observed in the cooling scan. When the glassy sample was heated again, the glass-transition phenomenon was observed at 84°C, and on further heating an exothermic peak due to crystallization

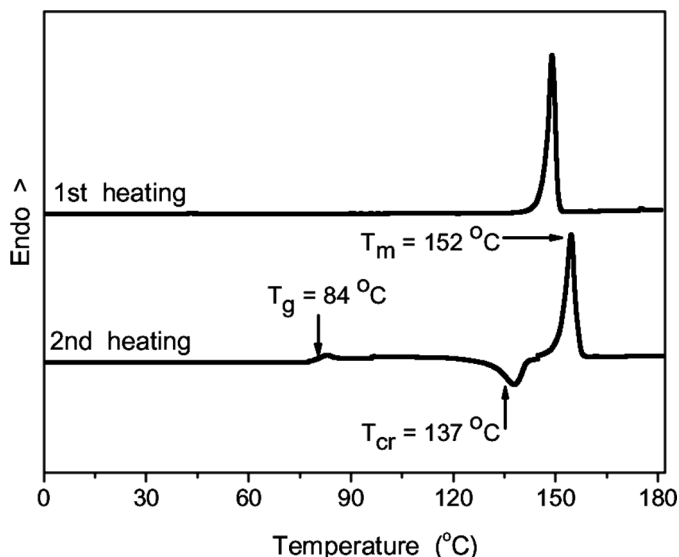


FIGURE 1 DSC curves of **8**. Heating rate: 10°C/min.

at 137°C and an endothermic peak due to melting at 152°C were observed.

UV absorption (Fig. 2) and FL spectra of dilute solutions of compounds **7–9** were recorded. The electronic absorption energy of these compounds is similar, and the λ_{max} values are in the range of 230–315 nm. Their FL emission maxima appear at 530, 497 and 443 nm for **7**, **8** and **9**, respectively. The absorption bands of the lowest energy and the photoluminescence band of the compound **7** having di(9-alkylcarbazol-3-yl)amino moieties attached to phenyltriazine core are slightly red shifted with respect of the corresponding bands of compound **8**, in which ditolylamino fragments are linked by phenyltriazine. The bathochromic shifts indicate that the 9-alkylcarbazol-3-yl groups make a considerable effect on the conjugation of molecules of the compounds, and a solid layer of the material **7** is expected to show lower ionization potential (I_p) than that of material **8**. The lowest energy absorption bands of the symmetric compound **9** are similar with respect of the corresponding bands of derivative **7**, however FL emission maxima of **9** is blue shifted to 443 nm. This observation indicates that conjugations between the central triazine ring and the substituents in the compound **9** are rather small due to the steric hindrance of ditolylamino substituents.

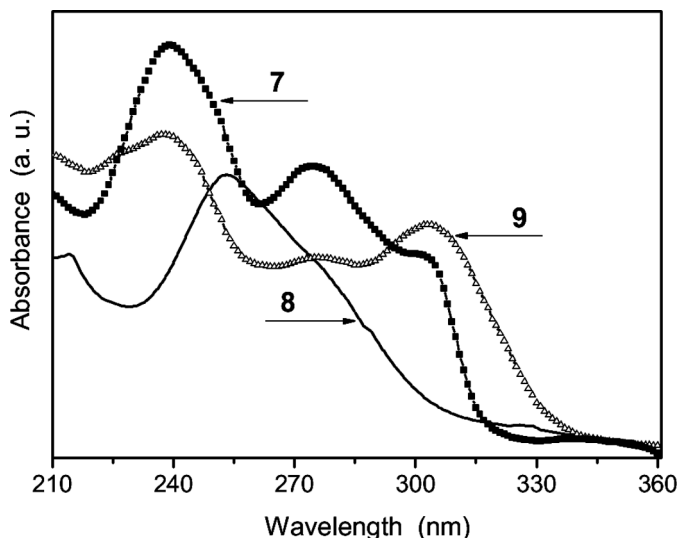


FIGURE 2 UV absorption spectra of the derivatives (**7–9**).

The electron photoemission spectra of films of compounds **7–9** are presented in Figure 3. The values of I_p for the films of compounds are 5.36, 5.83 and 5.97 eV for **7**, **8** and **9**, respectively. As it could be expected from UV and FL data, I_p of the compound **7** having di(9-alkyl-carbazol-3-yl)amino substituents is lower than of the ditolylamino-substituted triazines (**8–9**).

Material **7** is potential charge transporting component for electroluminescent devices. I_p of amorphous layers prepared using **7** is rather close to that of indium-tin oxide (ITO), which is widely used as anode in the latter devices [17]. The injection barrier of holes from the electrode into the layers of **7** would be ca 0.5 eV. The layers of **7–8** could also be applied for electrophotographic photoreceptors. Holes would be easily injected into their layers from a charge generation layer or a conductive anode with I_p or work function close to 5.3–5.8 eV. The I_p values for charge generation materials, including those widely used in electro-photographic photoreceptors pigments, such as titanyl phthalocyanines [18,19], perylene pigments [20] and bisazo pigments [21] are in the range of 5.1–5.6 eV.

The compounds **7–8** having the suitable I_p values and good solubility in PC-Z solutions were used for preliminary charge carrier mobility studies. Time of flight measurements were used to characterise the magnitude of the charge drift mobility for the materials dispersed in the latter polymeric binder (Fig. 4).

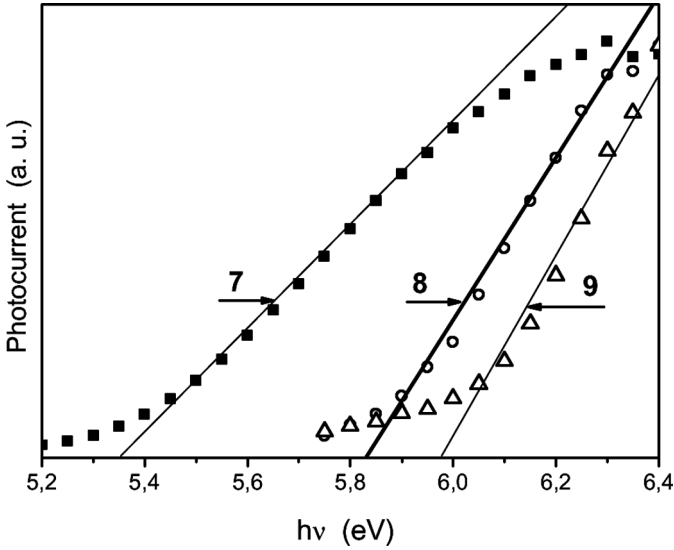


FIGURE 3 The electron photoemission spectra of the compounds **7–9**.

The experiments revealed that hole transport is characteristic for the materials **7–8** dispersed in PC-Z. The room temperature hole drift mobility shows a linear dependence on the square root of the electric

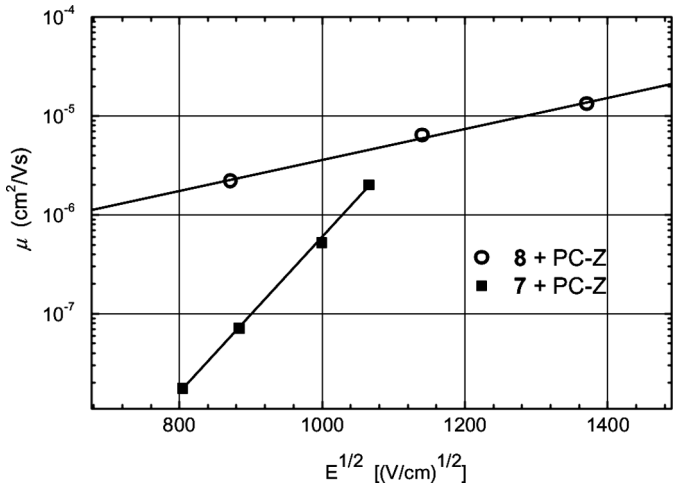


FIGURE 4 The electric field dependencies of the hole drift mobility in charge transport layers of the materials **7** and **8** doped in PC-Z (50%).

field in films of the compositions. This characteristic dependence is observed for the majority of non-crystalline organic systems and can be attributed to the effects of disorder on charge transport [22]. The PC-Z compositions with **7** or **8** demonstrated hole drift mobility values reaching $2 \times 10^{-6} \text{ cm}^2/(\text{Vs})$ ($E = 1.1 \times 10^6 \text{ V/cm}$) or $1.4 \times 10^{-5} \text{ cm}^2/(\text{Vs})$ ($E = 1.9 \times 10^6 \text{ V/cm}$), respectively, at room temperature. These values are noticeably higher than those observed in layers of classical photoconductor poly(N-vinylcarbazole) [22].

In conclusion, we have synthesized new diarylamino-substituted 1,3,5-triazine derivatives, which exhibit good thermal stability and form amorphous films with glass transition temperatures exceeding 84°C . The values of ionisation potentials (5.3 eV–5.8 eV) and the preliminary hole drift mobility studies show that these materials are potential components for electrophotographic photoreceptors and electroluminescent devices.

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