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Synthesis and properties of glass-forming phenothiazine and carbazole adducts

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Abstract

Charge-transporting and photoluminescent phenothiazine and carbazole adducts were synthesized and their thermal, optical, photophysical and photoelectrical properties were studied. The materials synthesized were found to constitute glasses with glass transition temperatures in the range of 63–78 °C. Their initial weight loss temperatures range from 334 to 362 °C. Steady state and time-resolved fluorescence spectrometry techniques have revealed energy transfer in the adducts of carbazole and phenothiazine and the existence of excimer forming sites in the films of 3-(10-phenothiazinyl)-9-ethylcarbazole and 3-(9-carbazolyl)-9-ethylcarbazole. The electron photoemission spectra of the materials were recorded and the ionization potentials of 5.38–5.87 eV were established. Time-of-flight hole drift mobilities of carbazole twin compound molecularly dispersed in bisphenol *Z* polycarbonate (1:2 by weight) approach 2×10^{-5} cm^2/V s at high electric field.

Keywords: Carbazole; Phenothiazine; Fluorescence; Charge mobilities; Ionization potential

1. Introduction

Derivatives of carbazole are widely studied and used as charge-transporting and light-emitting materials for optoelectronic devices such as electrophotographic receptors and light-emitting diodes [1,2]. Phenothiazinyl-containing compounds have been studied for these applications to a lesser extent, however, recently they attract increasing attention [3,4]. Both classes of materials have their own advantages. Compounds containing carbazole chromophores exhibit high mobilities of positive charges (holes) and high photoluminescence quantum yields. In addition some derivatives of carbazole possess high triplet energies and have been successfully used in blue electrophosphorescent devices [5]. Phenothiazine-based materials exhibit enhanced solubility in organic solvents and ability to form amorphous films on substrates. It was of interest to synthesize molecules having both carbazole and phenothiazine moieties. In this presentation we report on the synthesis and properties of carbazole and phenothiazine adducts. For the comparison the carbazole and phenothiazine twin molecules have been synthesized and studied.

2. Experimental

2.1. Materials

9*H*-Carbazole, 10*H*-phenothiazine, iodoethane, tetrabutylammonium hydrogensulphate, potassium hydroxide, sodium hydroxide, bromine, copper, potassium carbonate, 18-crown-6, potassium iodide, potassium iodate were purchased from Aldrich and used as received. 10-Ethylphenothiazine (**2**) was prepared by alkylation of 10*H*-phenothiazine with iodoethane, in the presence of a phase transfer catalyst using similar procedure as it was described earlier [6]. 3-Iodo-9*H*-carbazole (**4**)

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was obtained by the procedure of Tucker [7]. 3-Iodo-9-ethylcarbazole (**5**) was prepared by alkylation of 3-iodo-9*H*-carbazole (**4**) in the presence of a phase transfer catalyst by the procedure described earlier [8].

*2.1.1. 1-(10-Phenothiazinyl)-10H-phenothiazine (**1**)*

It was synthesized by the reported procedure [9]. 10*H*-Phenothiazine (10 g, 50.18 mmol) was dissolved in a mixture of 100 ml of DMSO and Ac_2O (2:1 (volume parts)) and stirred at room temperature for one week. Then the reaction mixture was poured into water. The aqueous phase was separated from the organic phase and extracted with ether. The combined organic phases were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the crude product was further purified by silica gel column using ether/hexane (volume ratio 1:2) as an eluent. Compound **1** was recrystallized from the eluent to yield 7.9 g (79%) of crystals (mp: 180−181 °C) (FW = 396.52 g/mol). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 6.24−6.30 (m, 2H, ar); 6.75−7.95 (m, 13H, ar); 8.93 (s, 1H, NH). IR (in KBr) ν/cm^{-1}: 3357 (NH); 3062 (CH_{ar}); 1591, 1571 ($C{=}C_{ar}$); 1303 (CN). MS ($APCI^+$, 20 V), *m*/*z*, (%): 397 ($[M+H]^+$, 40).

*2.1.2. 3-Bromo-10-ethylphenothiazine (**3**)*

It was prepared by the procedure similar to that reported earlier [10]. Sodium hydroxide (0.53 g, 13.2 mmol) was dissolved in glacial acetic acid (40 ml) under an atmosphere of nitrogen. 10-Ethylphenothiazine (1 g, 4.4 mmol) (**2**) was dissolved in 5 ml of chloroform and the solution obtained was added to the solution of sodium hydroxide in acetic acid. Then 0.11 ml (2.2 mmol) of bromine was dissolved in glacial acetic acid (10 ml) and added drop-wise to the reaction mixture at 5−10 °C. The reaction mixture was stirred at room temperature for 1 h and then poured into 100 ml of 5% aqueous solution of sodium hydroxide. The organic phase was separated from the aqueous phase and extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$. After filtration and rotary evaporation of the solvent, the crude product was further purified by silica gel column chromatography using an eluent mixture of ethylacetate and hexane in a volume ratio of 1:13. Compound **3** was recrystallized from a mixture of ethylacetate and methanol (volume ratio 1:3). The yield was 0.5 g (37%) of white crystals (mp: 122−124 °C). (FW = 306.22 g/mol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.44 (t, $J = 6.9$ Hz, 3H, CH_3); 3.91 (q, 2H, CH_2); 6.71−7.30 (m, 7H, ar). IR (in KBr) ν/cm^{-1}: 3080, 3053 (CH_{ar}); 2973, 2935, 2862 ($CH_{aliphatic}$); 1587, 1561 ($C{=}C_{ar}$); 1250 (C−N). MS ($APCI^+$, 20 V), *m*/*z*, (%): 308 ($[M+H]^+$, 75).

*2.1.3. 1-(10-Phenothiazinyl)-10-ethylphenothiazine (**6**)*

It was prepared by the procedure similar to that reported earlier [6]. 1-(10-Phenothiazinyl)-10*H*-phenothiazine (**1**) (1 g, 2.52 mmol), 0.6 g (3.83 mmol) of iodoethane and 0.016 g (0.046 mmol) of tetrabutylammonium hydrogensulphate were dissolved in toluene (30 ml). Potassium hydroxide (0.21 g, 3.83 mmol) was added stepwise and the reaction mixture was refluxed for 12 h. Then unreacted potassium hydroxide and inorganic salts were removed from the reaction mixture by filtration. The crude product was further purified by silica gel column chromatography using an eluent mixture of diethyl ether and hexane in a volume ratio of 1:2. The yield of amorphous powder of **6** was 0.7 g (65%). (FW = 424.59 g/mol).^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.53 (t, $J = 6.9$ Hz, 3H, CH_3); 4.03 (q, $J = 6.9$ Hz, 2H, CH_2); 6.3 (dd, $J = 7.9$ Hz, $J = 1.6$ Hz, 2H, ar); 6.80−7.2 (m, 153H, ar). IR ν_{max} (KBr): 3057 (CH_{ar}); 2973 ($CH_{aliphatic}$); 1591, 1571 ($C{=}C_{ar}$); 1232 (C−N). MS ($APCI^+$, 20 V), *m*/*z*, (%): 423 ($[M+H]^+$, 100).

*2.1.4. 3-(9-Carbazolyl)-10-ethylphenothiazine (**7**)*

A mixture of 0.55 g (3.29 mmol) of 9*H*-carbazole, 1 g (3.27 mmol) of 3-bromo-10-ethylphenothiazine (**3**), potassium carbonate powder 1.8 g (13 mmol), copper powder 0.41 g (6.5 mmol), 18-crown-6 0.09 g (0.34 mmol) in *o*-dichlorobenzene (20 ml) was refluxed 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 chromatography using an eluent mixture of diethyl ether and hexane in a volume ratio of 2:1. The yield of amorphous powder of **7** was 0.6 g (66%). (FW = 392.53 g/mol).^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.52 (t, $J = 6.9$ Hz,3H, CH_3); 4.5 (q, $J = 6.9$ Hz, 2H, CH_2); 6.9−8.2 (m, 15H, ar). IR ν_{max} (KBr): 3053 (CH_{ar}); 2976 ($CH_{aliphatic}$); 1625, 1597, 1577 ($C{=}C_{ar}$); 1230 (C−N). MS ($APCI^+$, 20 V), *m*/*z*, (%): 393 ($[M+H]^+$, 100).

*2.1.5. 3-(10-Phenothiazinyl)-9-ethylcarbazole (**8**)*

A mixture of 0.6 g (3.1 mmol) of 10*H*-phenothiazine, 1 g (3.11 mmol) of 3-iodo-9-ethylcarbazole (**5**), 1.7 g (12.5 mmol) potassium carbonate powder, 0.4 g (6.2 mmol) copper powder, 0.08 g (0.3 mmol) 18-crown-6 in *o*-dichlorobenzene (20 ml) was refluxed 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 chromatography using an eluent mixture of chloroform and hexane in a volume ratio of 1:5. Compound **8** was recrystallized from a mixture of solvents used as an eluent to yield 0.8 g (66 %) of yellow crystals (mp: 231−232 °C). (FW = 392.53 g/mol).^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.55 (t, $J = 7.2$ Hz, 3H, CH_3); 4.5 (q, $J = 7.2$ Hz, 2H, CH_2); 6.2−8.2 (m, 15H, ar). IR ν_{max} (KBr): 3058 (CH_{ar}); 2973 ($CH_{aliphatic}$); 1598, 1572, 1511 ($C{=}C_{ar}$); 1229 (C−N). MS ($APCI^+$, 20 V), *m*/*z*, (%): 393 ($[M+H]^+$, 100).

*2.1.6. 3-(9-Carbazolyl)-9-ethylcarbazoe (**9**)*

A mixture of 0.69 g (4.13 mmol) of 9*H*-carbazole, 2 g (6.23 mmol) of 3-iodo-9-ethylcarbazole (**5**), potassium carbonate powder 2.35 g (17 mmol), copper powder 0.53 g (8.3 mmol), 18-crown-6 0.11 g (0.42 mmol) in *o*-dichlorobenzene (30 ml) was refluxed 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 chromatography using an eluent mixture of chloroform and hexane in a volume ratio of 1:5. Compound **9** was recrystallized from the eluent mixture of solvents to yield 1.16 g (78%) of white crystals (mp: 204–205 °C). (FW = 360.46 g/mol). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.57 (t, $J = 7.6$ Hz, 3H, CH_3); 4.48 (q, $J = 7.2$ Hz, 2H, CH_2); 7.24–7.66 (m, 12H, ar); 8.10 (d, $J = 7.6$ Hz, 1H, ar); 8.21 (d, $J = 7.6$ Hz, 1H, ar); 8.27 (s, 1H, ar). IR ν_{max} (KBr): 3048 (CH_{ar}); 2980 ($CH_{aliphatic}$); 1623, 1592, 1571 ($C{=}C_{ar}$); 1229 (C–N). MS ($APCI^+$, 20 V), *m/z*, (%): 361 ($[M + H]^+$, 42).

2.2. Methods

^{1}H NMR spectra were recorded using Varian Unity Inova (300 MHz) spectrometer. All the data are given as chemical shifts δ (ppm) downfield from $Si(CH_3)_4$.

IR spectra were recorded using Perkin Elmer FT-IR System. The spectra of the solid compounds were performed in the form of KBr pellets. Mass spectra were obtained on a Waters ZQ 2000.

UV spectra of 10^{-5} M solutions of the synthesized compounds in THF were recorded on a Spectronic Unicam Genesys-8 spectrometer using a microcell with an internal width of 1 mm.

Steady state fluorescence spectra were recorded with a MPF-4 spectrometer.

Fluorescence lifetime data were acquired on an IBH System 5000 or an Edinburgh Instruments 199 spectrometers operating under time-correlated single photon counting conditions. IBH System 5000 spectrometer employed a nanosecond thyratron-gated coaxial flashlamp (with H_2 as discharge medium) used as pulsed excitation source. The MHz repetition-rate excitation source was either an IBH Nano-LED-N15 (for 279 nm excitation) or an IBH Nano-LED-N16 (for 338 nm excitation) in Edinburgh Instruments 199 spectrometer. The decay curves were analyzed using a multiexponential fitting software provided by manufacturer. χ^2 values and weighted residuals were used as the goodness-of-fit criteria. Fluorescence lifetime measurements were made at room temperature on air-saturated THF solutions and thin films of the compounds. In order to avoid spectra distortion by reabsorption, the solutions were diluted to give an absorbance of 0.1 or less at the excitation wavelength. The concentration of the solution was 10^{-5} mol l^{-1}. The thin films of the compounds were prepared by casting on quartz glass from the dichlormethane solutions. Traces of solvent were removed by drying at reduced pressure at room temperature over a period of several days.

Differential scanning calorimetry (DSC) measurements were carried out with 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.

Melting points were measured on a MEL-TEMP (Electrothermal) melting point apparatus.

The ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission in air method as described before [11].

Hole drift mobilities were measured by a xerographic time-of-flight (XTOF) method [12–14]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the mixtures of the synthesized compounds with bisphenol *Z* polycarbonate (PC-*Z*) on polyester films with Al layer. The thickness of the charge-transporting layers varied in the range of 6–10 μm.

3. Results and discussion

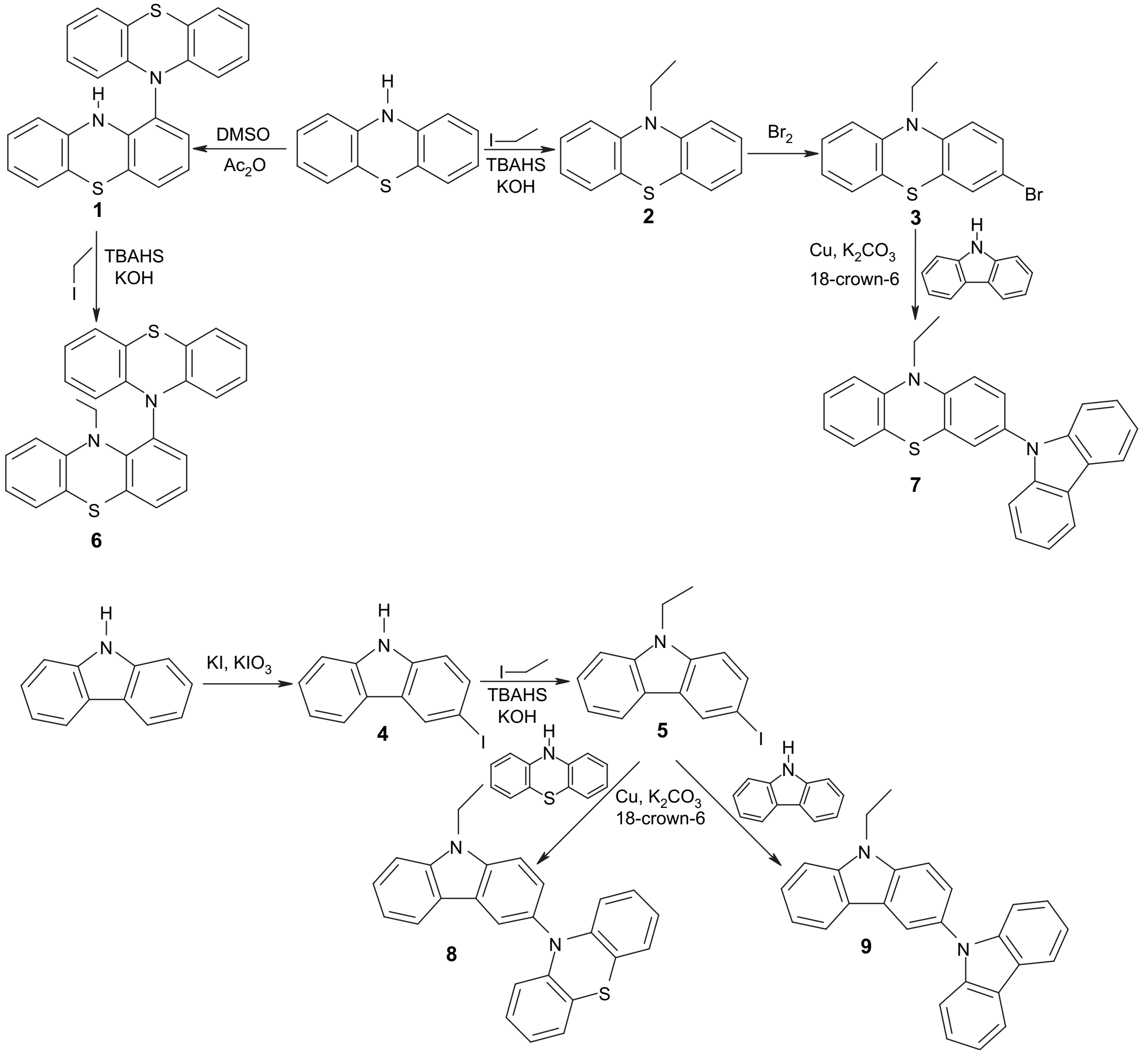
Phenothiazinyl- and carbazolyl-containing compounds (**7**–**9**) were synthesized as described in Scheme 1 via Ullmann coupling reaction of 3-iodo-9-ethylcarbazole (**5**) or 3-bromo-10-ethylphenothiazine (**3**) with of 9*H*-carbazole or 10*H*-phenothiazine. The bromo-derivative (**3**) was prepared by alkylation of 10*H*-phenothiazine and following bromination with bromine. The iodo-derivative (**5**) was prepared by alkylation of 3-iodo-9*H*-carbazole (**4**) which was synthesized by the Tucker [7] iodination of 9*H*-carbazole in the presence of KI and KIO_3. Compound **6** was prepared by alkylation of 1-(10-phenothiazinyl)-10*H*-phenothiazine (**1**) which was synthesized by oxidation of 10*H*-phenothiazine in a mixture of DMSO and Ac_2O according to the earlier reported procedure [9].

All the synthesized compounds were identified by IR, ^{1}H NMR and mass spectrometry measurements. The data were found to be in good agreement with the proposed structures. All the phenothiazinyl- and carbazolyl-containing compounds were readily soluble in common organic solvents, such as tetrachloroethane, chloroform, THF and acetone at room the temperature.

The behaviour under heating of compounds **6**–**9** was studied by DSC and TGA under a nitrogen atmosphere. The values of glass transition temperatures (T_g) and temperatures at which initial loss of mass was observed (T_{ID}) are summarized in Table 1. All the derivatives demonstrate relatively high thermal stability. The mass loss occurs at the temperatures higher than 334 °C, as confirmed by TGA with a heating rate of 10 °C/min.

Derivatives **6** and **7** were obtained as amorphous materials as confirmed by DSC. When the samples were heated the glass transitions were observed at 78 and 63 °C, respectively, and no peaks due to crystallization and melting appeared.

Carbazolyl-based compounds **8**, **9** were isolated after the synthesis as crystalline compounds, however, they formed glass when the melt samples were cooled down. The DSC thermograms of **8** are shown in Fig. 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 232 °C. When the melt sample was cooled down and heated again, the glass transition was observed at 72 °C, followed by exothermic crystallization signal at 156 °C and melting signals at 225 and 232 °C. The melting behaviour of the sample obtained by the crystallization from solution observed in the first heating scan is different from that observed in the second heating scan for the sample



Scheme 1.

crystallized from the melt. Two melting peaks observed in the second heating scan at 225 and 232 °C are apparently conditioned by polymorphism. This is not the first observation of polymorphism for the low-molar-mass glass-forming compounds. Earlier the different crystalline forms for the glass-forming molecular materials were reported by Shirota [15].

The synthesized aromatic amines were also studied by UV–vis and fluorescence spectrometry measurements. UV absorption spectra of the dilute solutions are shown in Fig. 2. For the comparison the spectra of 10-ethylphenothiazine (EtPH) and 9-ethylcarbazole (EtCz) are also shown. The solutions

Table 1
Thermal characteristics of compounds **6–9**

Compound	T_m (°C)	T_g (°C)	T_{ID} (°C)
6	–	78	362
7	–	63	359
8	225, 232	72	334
9	205	75	336

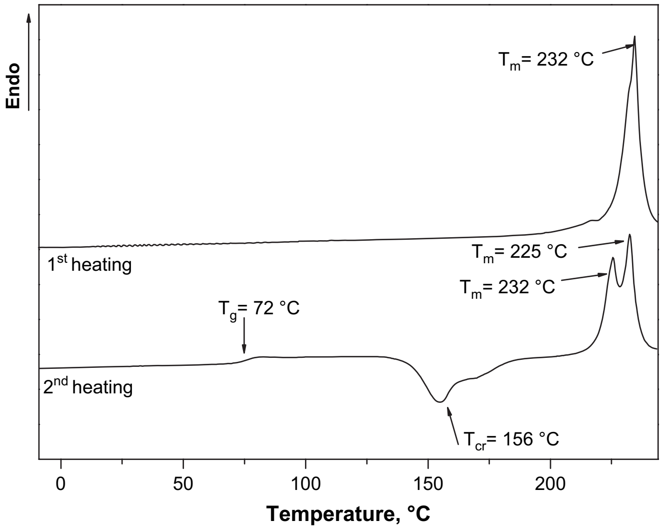


Fig. 1. DSC curves of compound **8**, at the heating rate of 10 °C/min, N_2 atmosphere.

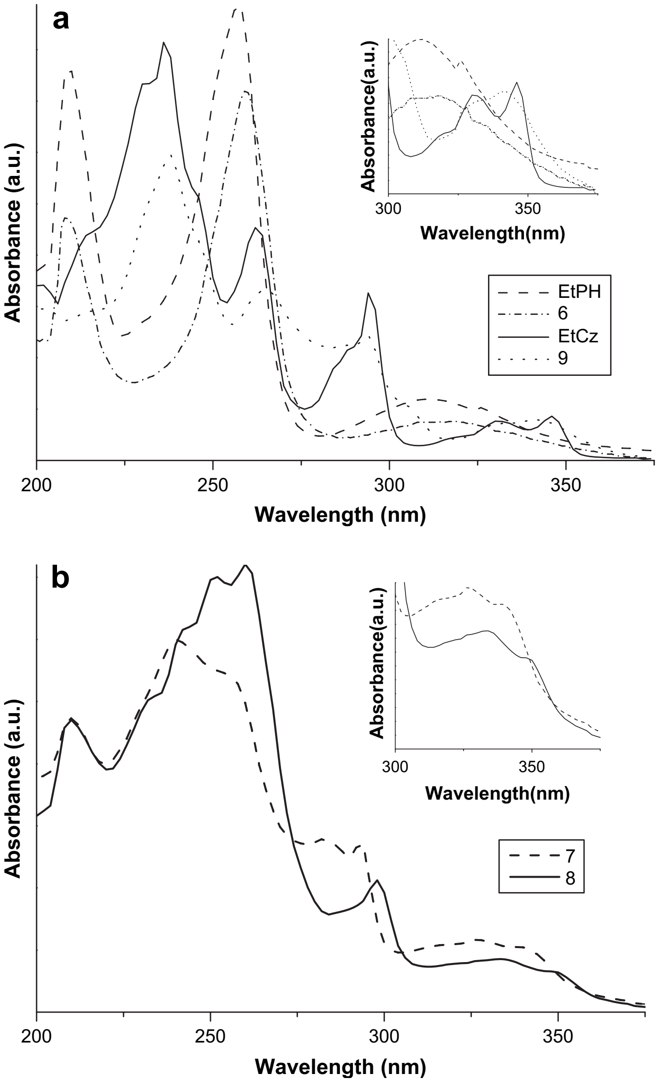


Fig. 2. UV absorption spectra of the dilute THF solutions (10^{-5} mol l^{-1}) of compounds: (a) **6**, **9**, 10-ethylphenothiazine (EtPH) and 9-ethylcarbazole (EtCz); (b) **7**, **8**.

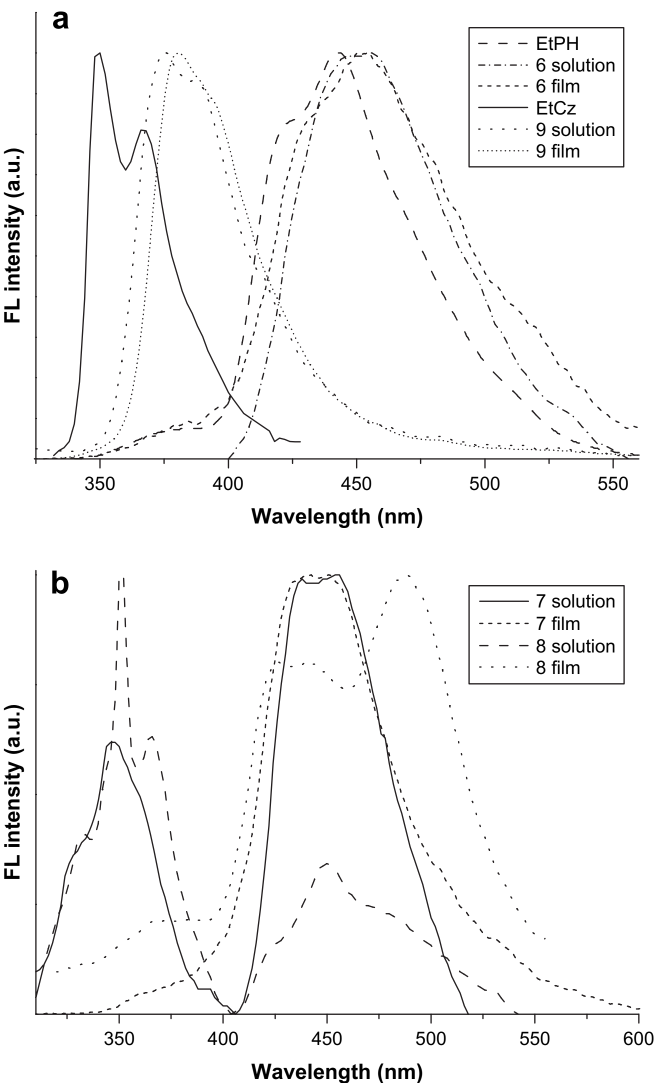


Fig. 3. Fluorescence spectra of compounds: (a) **6**, **9**, 10-ethylphenothiazine (EtPH) and 9-ethylcarbazole (EtCz); (b) **7**, **8**. For **6**–**9** (solutions, films) $\lambda_{ex} = 290$ nm, for EtPH $\lambda_{ex} = 310$ nm, for EtCz $\lambda_{ex} = 330$ nm.

of compounds **6**–**9** exhibit a broad absorption with the absorption maxima in the range of 210–360 nm. The spectra of the synthesized phenothiazine and carbazole dimers **6** and **9** exhibit absorption bands of phenothiazine and carbazole moieties, respectively (Fig. 2a). The spectrum of **6** resembles that of EtPH, while the spectrum of **9** resembles the spectrum of EtCz. This observation shows that the interaction between the chromophores in these molecules is rather week. The comparison of the UV spectra of 3-(9-carbazolyl)-10-ethylphenothiazine (**7**) and 3-(10-phenothiazinyl)-9-ethylcarbazole (**8**) (Fig. 2b) with those of EtCz or EtPH (Fig. 2a), shows that the absorption peaks characteristic of both carbazole and phenothiazine chromophores are present in the spectra of these compounds. The absence of any other peaks and the fact that the spectrum is a superposition of the peaks of separate chromophores indicate low electronic interactions in the ground state of the molecules of **7** and **9** in the solution.

Fluorescence spectra of compounds **6**–**9** are shown in Fig. 3. For the comparison the corresponding spectra of EtPH and EtCz are given. The fluorescence band of compound **6** is red shifted by ca. 13 nm with respect of the fluorescence band of EtPH and the spectrum of **9** is red shifted by ca. 25 nm with respect of the spectrum of EtCz. These observations show that there are certain interactions between the chromophores in phenothiazine and, especially, carbazole dimers (**6** and **9**, respectively) in the excited state. The fluorescence spectra of the films of compounds **6** and **9** are similar to those of the dilute solutions. However, broadening of the fluorescence band extending over 500 nm was observed for carbazole dimer. The structureless 'tail' of the emission band of the film of **9** could be assigned to that resulting from the formation of an intermolecular excimer in which two carbazole groups have achieved an overlapping. Also the existence of the higher energy excimer forming sites in both dilute solution and thin film of **9**, giving structureless emission peaking at about 380 nm, cannot be excluded [16].

The emission bands of both carbazole and phenothiazine chromophores are present in the fluorescence spectra of the dilute solutions of compounds **7** and **8**. The relative intensity of the emission band of carbazole chromophore is decreased in the fluorescence spectrum of dilute solution of **7** apparently due to the energy transfer from carbazole to phenothiazine groups. The energy transfer is much more evident in the films of the compounds. The fluorescence spectra of the amorphous films of compounds **7** and **8** exhibit almost no emission from carbazole chromophores. The fluorescence peak of compound **7** coincides with that of EtPH, which shows that emission of unassociated phenothiazine moieties is characteristic of the film of **7**. The fluorescence spectrum of the film of compound **8** consists of two main emission components. The first emission band is centered at 450 nm and it is conditioned by the emission of phenothiazinyl group. The second is higher intensity band at around 500 nm which can apparently be assigned as that from the formation of intermolecular excimers in the film of **8**.

The fluorescence decay dynamics of compounds **6**–**9** in dilute THF solutions and thin films were examined by monitoring their characteristic emission maxima and excitation beam at several different wavelengths was employed. The fluorescence decay curves of compounds **8** and **9** with the corresponding exponential fits are shown in Figs. 4 and 5, along with the decay data parameters for all molecules given in Table 2. The relative proportions of decay components at various excitation and emission wavelengths are also indicated. The analysis parameters show that fluorescence decay of the compounds can be adequately described by single or double exponential function. The low values of χ^2 (χ^2 has to be close to unity for good fit) and the random distribution of residuals provided confidence in the statistical quality of the analyses.

Two components are present in time-dependent fluorescence of the phenothiazine dimer **6**. The short living component gave dominant fluorescence lifetime of 1.6–1.9 ns and longer living component gave lifetime of 6.5 ns. The observed short lifetimes are within the range of values reported for 10-alkylated phenothiazine derivatives obtained under the same conditions [17]. The obtained fluorescence decay curves of carbazole dimer were best described by a monoexponential decay function (Fig. 4), giving a fluorescence lifetime of 4.5–4.6 ns for the dilute solutions of **9** in THF. The analysis of solid state fluorescence decay data of **9** (Fig. 5) at the emission band conditioned by "monomeric" carbazole (~400 nm), produced short lifetimes that are comparable to those of dilute solution of the molecules in THF. The obtained fluorescence decay curves at the emission wavelength characteristic for associated excited state carbazole (~500 nm) gave long lifetimes of ca. 20 ns. Also relatively long lifetimes at the latter wavelength were obtained for the thin film of **8**, indicating the formation of the intermolecular excited state complex in the mixed adduct. The fluorescence decay dynamics of the dilute solution of **8** was not monoexponential (Fig. 4), requiring two exponentials to achieve best fits of the data. The decay of the characteristic emission bands of compound **8** in THF was examined, giving short lifetimes in 1–5 ns range. The decay curves of **7** at two characteristic emission bands of 370 and 450 nm were best described by a single or double exponential decay function, giving fluorescence lifetime of 2–4 ns. It is worth to notice that the lifetime of the

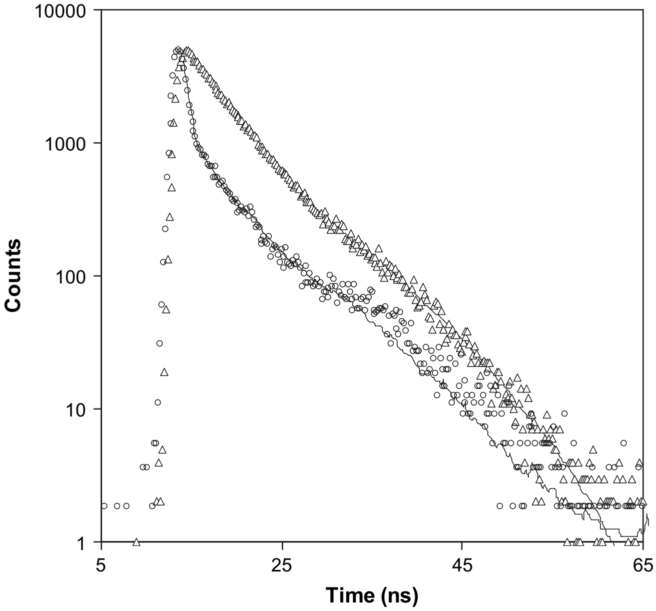


Fig. 4. Fluorescence decay curves ($\lambda_{em} = 370$ nm) of dilute solutions of **8** and **9** in THF (10^{-5} M) with the excitation of 279 nm. Open symbols represent the actual data and the solid lines are fits to the data. The decay of **8** (○) fitted to a dual-exponential model, the decay of **9** (△) fitted to a single-exponential model.

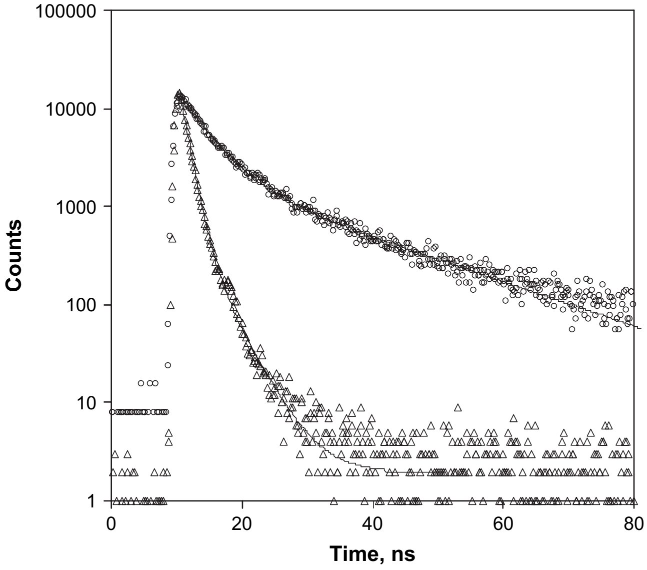


Fig. 5. Fluorescence decay curves of thin film of **9** with the excitation of 279 nm. Open symbols represent the actual data and the solid lines are fits to the data. The decay at 400 nm (△) and 500 nm (○) are fitted to a dual-exponential model.

Table 2
Fluorescence decay parameters resultant upon single or double exponential fitting to the time-resolved fluorescence of dilute solutions ($c = 10^{-5}$ M in THF) and thin films of compounds **6–9**

Sample	λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	χ^2
6 (in THF)	338	450	1.62 ± 0.01 (0.91)	6.59 ± 0.18 (0.09)	2.05
6 (film)	338	450	1.35 ± 0.02 (0.73)	6.20 ± 0.14 (0.27)	1.11
7 (in THF)	279	370	2.79 ± 0.18 (1)		3.34
		450	1.41 ± 0.02 (0.78)	4.03 ± 0.06 (0.22)	1.81
	338	370	2.38 ± 0.21 (1)		3.18
		450	1.36 ± 0.02 (0.72)	4.08 ± 0.05 (0.28)	1.57
7 (film)	338	450	1.04 ± 0.02 (0.79)	3.34 ± 0.15 (0.21)	1.10
8 (in THF)	279	370	0.37 ± 0.01 (0.57)	4.67 ± 0.06 (0.43)	1.05
		450	1.17 ± 0.07 (0.37)	4.38 ± 0.05 (0.63)	1.28
		500	4.69 ± 0.03 (1)		2.19
	338	370	0.76 ± 0.01 (0.84)	4.42 ± 0.36 (0.16)	2.84
		450	1.20 ± 0.05 (0.44)	4.89 ± 0.05 (0.56)	1.06
		500	4.42 ± 0.03 (1)		1.06
8 (film)	279	450	1.87 ± 0.05 (0.59)	6.05 ± 0.10 (0.41)	1.10
		500	4.89 ± 0.12 (0.47)	10.93 ± 0.11 (0.53)	1.28
	338	450	2.03 ± 0.05 (0.70)	8.77 ± 0.27 (0.30)	1.44
		500	5.01 ± 0.18 (0.53)	11.78 ± 0.20 (0.47)	1.20
9 (in THF)	279	370	4.53 ± 0.02 (1)		1.04
	338	370	4.66 ± 0.02 (1)		1.00
9 (film)	279	400	1.15 ± 0.01 (0.86)	3.52 ± 0.10 (0.14)	2.58
		500	4.09 ± 0.11 (0.51)	19.91 ± 0.62 (0.49)	1.75
	338	400	1.21 ± 0.02 (0.89)	3.67 ± 0.14 (0.11)	2.43
		500	4.00 ± 0.10 (0.51)	19.17 ± 0.58 (0.49)	1.52

"monomeric" carbazole (at 370 nm) for both mixed adducts **7** and **8** was slightly shorter compared to that of the carbazole dimer **9**. This observation can be apparently explained by the quenching of the emission of unassociated carbazolyl moieties due to energy transfer and/or the formation of intermolecular excimers in the samples of the mixed adducts.

Thus the time-resolved fluorescence spectrometry data support the steady state fluorescence spectrometry evidence about the existence of excited intermolecular dimers in the films of **8** and **9**, as well as the energy transfer in the mixed adducts **7** and **8**.

Fig. 6 shows electron photoemission spectra of the amorphous films of the materials synthesized. The values of I_p for the films of **6–9** are 5.9, 5.6, 5.4 and 5.7 eV, respectively. I_p values of compounds having two different chromophores (**7**, **8**) have appeared to be lower than those of the adducts having the uniform chromophores (**6**, **9**).

Time-of-flight measurements were used to characterize the magnitude of hole drift mobility (μ) for the synthesized materials molecularly dispersed in the polymer host bisphenol *Z* polycarbonate (PC-*Z*). The electric field dependencies of μ are given in Fig. 7. The solid solutions of **6–9** in PC-*Z* demonstrated hole drift mobility values in the range from 8×10^{-9} to 2×10^{-5} cm^2/V s at high electric fields at the room temperature. The highest charge mobilities were observed for the systems containing twin molecules **9** and **6** i.e. compounds with the uniform chromophores.

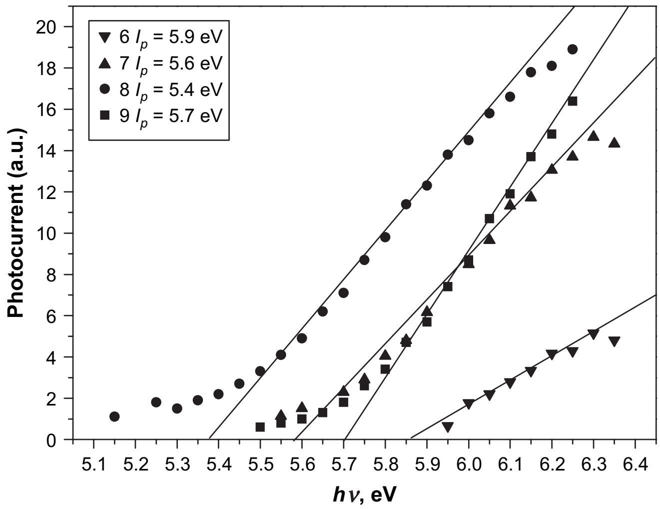


Fig. 6. Electron photoemission spectra of the films of compounds **6–9**.

In conclusion we have synthesized, characterized and studied a series of glass-forming hole transporting adducts of carbazole and phenothiazine. All the synthesized materials exhibit high thermal stabilities with the initial weight loss temperatures above 330 °C and form glasses with glass transition temperatures ranging from 63 to 78 °C. Steady state and time-resolved fluorescence spectrometry techniques have revealed energy transfer in the adducts of carbazole and phenothiazine and the existence of excimer forming sites in the films of 3-(10-phenothiazinyl)-9-ethylcarbazole. The ionization potentials of the synthesized materials range from 5.4 to 5.9 eV. Twin compounds i.e. 3-(9-carbazolyl)-9-ethylcarbazoe and 1-(10-phenothiazinyl)-10-ethylphenothiazine exhibit superior charge transport properties with respect of the "mixed"

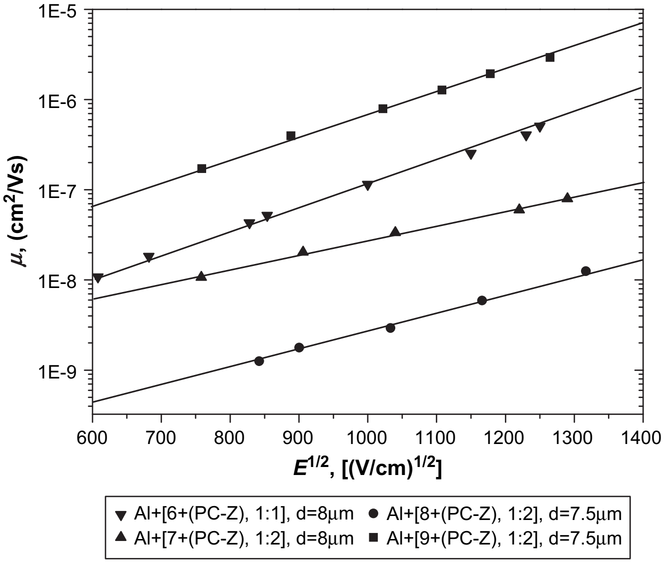


Fig. 7. Electric field dependencies of hole drift mobility (μ) in charge transport layer of compounds **6–9** doped in PC-*Z* (mass proportion 1:1 or 1:2).

adduct of carbazole and phenothiazine derivatives. Time-of-flight hole drift mobilities in the 25% solid solution of 3-(9-carbazolyl)-9-ethylcarbazole in bisphenol *Z* polycarbonate exceed 10^{-5} cm^2/V s at high electric fields.

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