Synthesis, photophysical and photoelectrical properties of glass-forming phenothiazinyl- and carbazolyl-substituted ethylenes

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Phenothiazinyl- and carbazolyl-substituted ethylenes have been synthesized and found to constitute electro-active materials with high thermal stability as characterised by thermo-gravimetric analysis. Steady state absorption and luminescence spectra of the synthesized derivatives were examined in detail revealing green-blue emission with efficiency ranging from 13 % to 28 %. Based on the emission spectra of the synthesized compounds Commission Internationale d'Eclairage (CIE) chromaticity coordinates have been obtained. Major luminescence decay time component of ~2.5 ns was determined in dilute solutions of the compounds, whereas significantly shorter one has been estimated in thin films. Electron photoemission spectra of the materials have been recorded and the ionisation potentials of 5.3-5.4 eV have been established. Room temperature hole drift mobilities of the diarylethylenes dispersed in polymeric host approached 10^{-5} cm^2/Vs at high electric fields.

1. Introduction

Organic amorphous materials exhibiting both charge transport and emission properties are of interest for the application in optoelectronic devices such as organic light emitting diodes [1]. Carbazale and phenothiazine derivatives are known to be capable of both transporting holes and emitting blue light after excitation [3-5]. Increase of the size of electroactive molecules usually reinforces their inclination to glass formation. In addition, if increase of the size of molecules is associated with increase of the systems of conjugated π-electrons, it leads to the change of emission properties. Various approaches of increase of the size of carbazoole or phenothiazine-based molecules have been used so far. Electroactive materials containing two or more carbazolyl or phenothiazinyl groups were prepared by oxidative coupling [6], Ni(0) coupling [7], Suzuki cross coupling [8], palladium catalysed reaction of ethynyl- and halogen derivatives [9], Wittig reaction [10], Ullmann condensation [11] etc. In this presentation we report on the synthesis of compounds containing two phenotiazinyl or carbazolyl grpups by McMurry reaction of the corresponding formyl derivatives and on investigation of the properties of the synthesized materials. Photophysical and photoelectrical properties are emphasized.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using Varian Unity Inova and JOEL JNM- FX 100 equipment. 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[TM] 8 spectrometer.

Steady state fluorescence spectra were measured on a Perkin Elmer LS50B luminescence spectrometer. Fluorescence lifetime data were acquired on an IBH System 5000 or an Edinburgh Instruments 199 spectrometers operating in the time-correlated single photon counting regime. 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 IBH Nano-LED-03 (for 370 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 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 0.2 or less (the concentration of the solutions was 10^{-5} mol/l) at the excitation wavelength. The solutions with even lower absorbance (<0.05) were used to estimate fluorescence quantum efficiency. Quantum efficiencies of the solutions of the synthesized compounds were estimated by comparing their spectrally integrated emission intensities with that of the standard [12]. Quinine sulphate dissolved in 0.1M H_2SO_4, and exhibiting 53±2.3 % quantum yield at an excitation wavelength of 366 nm [13] was used as a standard in these estimations. Different refractive indices of the standard and the solutions under investigation were taken into account.

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 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 we have described earlier [3]. The measurement method was, in principle, similar to that demonstrated by Miyamoto et al. [14].

The hole drift mobility was measured by the time of flight technique in electrophotographic regime [15]. The samples for the charge carrier mobility measurements were prepared by casting the materials dispersed in bisphenol Z polycarbonate (PC-Z) on glass plates with conductive SnO_2 layer or polyester films with Al layer. The thickness of the transporting layer varied in the range of 3-10 μm.

2.2. Materials

10H-phenothiazine, 4-iodoanisole, 9-ethylcarbazole and bromoalkanes were purchased from Aldrich and used as received.

10-(p-Methoxyphenyl)phenothiazine (**2**) was obtained by an improved Ullmann coupling reaction [16]. 29.9 g (0.13 mole) of 4-iodoanisole, 17 g (0.09 mole) of 10H-phenothiazine, 10.9 g (0.17 mole) of copper powder, 40.1 g (0.3 mole) of potassium carbonate and 2.2 g (0.01 mole) of 18-crown-6 in 50 ml of 1,2-dichlorobenzene were heated to 180 °C and reacted for 24 hours. The inorganic components were filtered of while hot and the product was recrystallized from chlorofom. Yield: 57 % of brown crystals. ^{1}H NMR (CDCl$_3$): δ= 3.87(s, 3H), 6.11-6.29(m, 4H), 6.71-7.38(m, 8H). IR (KBr), ν/cm^{-1}: 3060, 2948,

1606, 1590, 1511, 1433, 1299, 1249, 1031, 743. MS: m/z = 306 (M+1).

10-(2-Ethylhexyl)phenothiazine was prepared by alkylation of 10H-phenothiazine in the presence of a phase transfer catalyst [17].

3-Formyl-10-(p-methoxyphenyl)phenothiazine (**3**), *3-formyl-10-(2-ethylhexyl)phenothiazine* and *3-formyl-9-ethylcarbazole* were synthesized by Vilsmeier reaction [18] of corresponding heterocyclic derivatives.

1,2-di[10-(p-methoxyphenyl)phenothiazin- 3- yl]ethylene (**4**) was prepared via McMurry coupling reaction [19]. TiCl$_4$ 0.6 ml (5.27 mmol) was added drop-wise to a stirred suspension of zinc powder 0.68 g (10.41 mmol) in freshly distilled anhydrous THF (10 ml) at -10 °C under the protection of nitrogen. The resulting dark mixture was heated under reflux for 1h. The suspension was cooled to 20 °C and 3-formyl-10-(p-methoxyphenyl)phenothiazine (1.83 g, 5.48 mmol) was added slowly. Reflux was continued for 4h under nitrogen. The resulting mixture was poured into 10% aqueous K_2CO_3 solution and the aqueous layer was extracted with ether. The combined organic extracts were dried and evaporated to give a yellow powder. The crude product was purified by column chromatography on silica gel using hexane/ ethylacetate (vol. ratio 5:1) as eluent. After recrystallizatio from metanol compound **4** in 45 % yield was obtained. M.p. 155-156 °C. ^{1}H NMR (CDCl$_3$): δ= 3.92(s, 6H), 6.1-7.36(m, 24H). IR (KBr), ν/cm^{-1}: 3340, 3053, 1888, 1595, 1571, 1474, 1443, 1312, 1034, 934, 925, 885, 860, 739. MS: m/z = 636(M+1), 635 (M$^+$), 580, 496, 478, 394.

1,2-di[10-(2-ethylhexyl)phenothiazin-3-yl]ethylene (**5**) was prepared from 1.86 g (5.48 mmol) of 3-formyl-10-(2-ethylhexyl)phenothiazine in the same way as product **4**. The compound was purified by column chromatography on silica gel using hexane/ ethyl acetate (vol. ratio 10:1) as eluent to obtain compound 5 in 34 % yield. ^{1}H NMR (CDCl$_3$): δ= 0.92-1.02(m, 12H), 1.24-1,55(m, 16H) 1.96-2.07(m, 2H), 3.91(d, 4H), 6.91-7.46(m, 16H). IR (KBr), ν/cm^{-1}: 3430, 3059, 2926, 1599, 1576, 1495, 1462, 1328, 1249, 1104, 957, 927, 877, 850, 815, 745. MS: m/z = 647 (M+1), 493, 451, 441, 350, 305.

1,2-di[9-ethylcarbazol-3-yl]ethylene (**6**) was prepared from 1.22 g (5.48 mmol) of 3-formyl-9-ethylcarbazole in the same way as product **4**. The compound was purified by column chromatography on silica gel using hexane/ ethyl acetate (vol. ratio 10:1) as eluent to obtain compound **6** in 88 % yield. ^{1}H NMR (CDCl$_3$): δ= 1.34-1.47(m, 6H), 4.18-4.49(m, 4H), 7.17-8.38(m, 16H). IR (KBr), ν/cm^{-1}: 3435, 3047, 2973, 1600, 1490, 1380, 1331, 1232, 1152, 959, 939, 884, 806, 770, 747. MS: m/z = 415.5 (M+1), 403, 334, 239, 209, 196.

3. Results and discussion

The basic strategy employed for the synthesis of 1,2-diarylethylenes was based on McMurry coupling reaction [19]. The synthetic route to 1,2-di[10-(p-

methoxyphenyl)phenothiazin-3-yl]ethylene (**4**) is illustrated in Scheme 1. Compound **4** was prepared via the McMurry coupling of 3-formyl-10-(p-methoxyphenyl)phenothiazine (**3**). The aldehyde **3** was obtained by Vilsmeier formylation [8] of 10-(p-methoxyphenyl)phenothiazine (**2**) which was synthesized by Ullmann coupling reaction of 10H-phenothiazine (**1**) with an excess of 4-iodoanisole. 1,2-Di[10-(2-ethylhexyl)phenothiazin-3-yl]ethylene (**5**) and 1,2-di[9-ethylcarbazol-3-yl]ethylene (**6**) were prepared using the same method from 10-(2-ethylhexyl)phenothiazine and 9-ethylcarbazole, respectively.
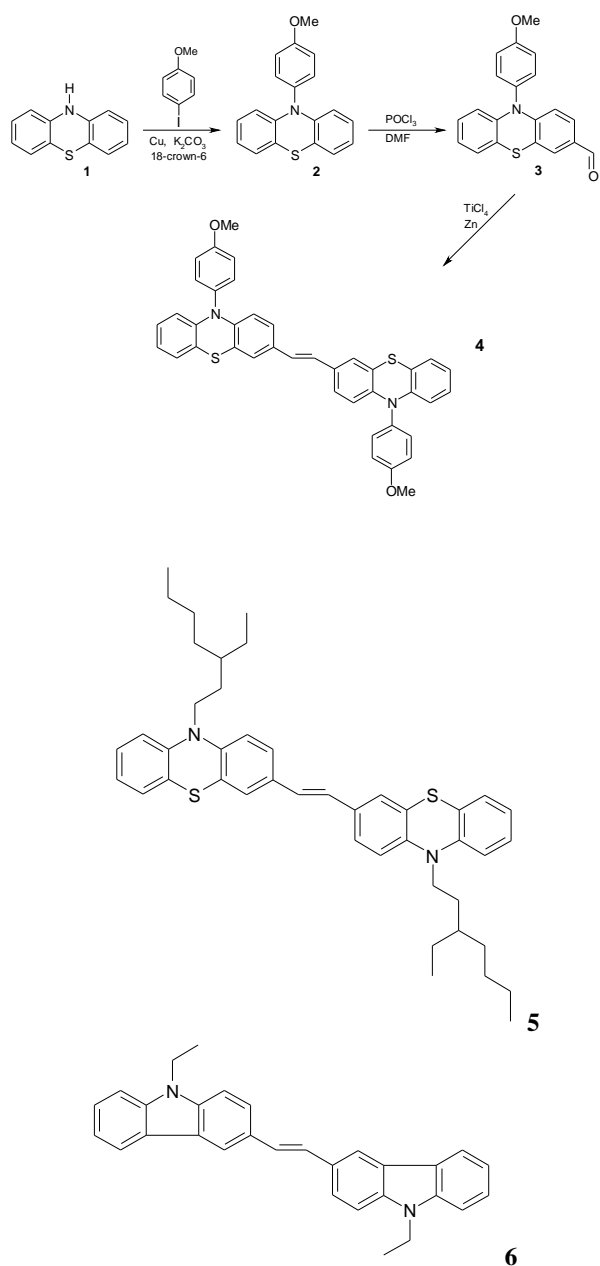
Scheme 1.

All the synthesized compounds were identified by mass spectrometry, IR and electronic ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. *Trans* isomers are usually obtained by McMurry coupling [20].

The aryl substituted ethylenes (**4 - 6**) were readily soluble in common organic solvents, such as tetrachloroethane, chloroform, THF and acetone at the room temperature.

The behaviour under heating of compounds **4 - 6** was studied by TGA and DSC under a nitrogen atmosphere. The values of the glass transition temperatures (T_g) and the temperatures at which initial loss of mass was observed (T_{ID}) are summarised in Table 1. All the derivatives demonstrate high thermal stability. The mass loss occurs at the temperatures higher than 315 ^{o}C, as confirmed by TGA with a heating rate of 10 ^{o}C/min.

Table 1. Thermal characteristics of compounds 4 – 6.

Compound	T_g (^{o}C)	T_{ID} (^{o}C)
4	33	315
5	17	361
6	128	364

It is evident that compound **4** having methoxyphenyl substitutent at the nitrogen atom of phenothiazinyl group exhibits lower thermal stability than the similar compound with alkyl substituents (**5**). On the other hand, the thermal stability the compounds seems not to depend on the heteroaromatic substituent at ethylene group (compounds **5** and **6** show similar T_{ID} values).

Compound **4** was isolated in a form of polycrystals by crystallisation from solution, however it readily formed glass when the melt sample was cooled. The DSC thermograms of **4** are shown in Fig. 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 157 ^{o}C. When the melt sample was cooled down and heated again, the glass-transition phenomenon was observed at 33 ^{o}C and on further heating no peaks due to crystallisation and melting appeared.
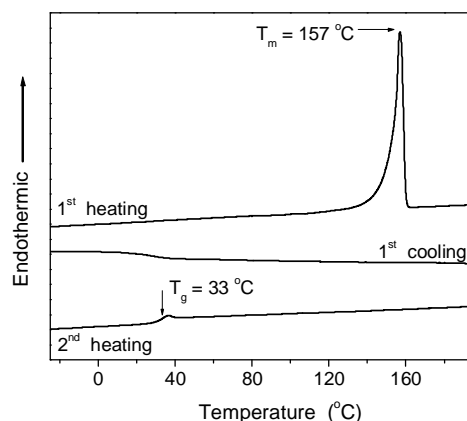

Fig. 1. DSC curves of the material 4. Heating rate: 10° C/min.

The derivatives **5** and **6** were obtained in nature as amorphous materials as confirmed by DSC. When the samples were heated the glass-transitions were observed at 17 and 128 $^{\circ}$C, respectively, and no peaks due to crystallization and melting appeared. The values of T_g of the phenothiazinyl- based ethylenes **4** and **5** show that their solid state properties can be examined only when the materials are dispersed in a polymeric host.

Absorption spectra of dilute solutions of the diarylethylenes are presented in Fig. 2. For comparison the corresponding spectra of 10-(2-ethylhexyl)phenothiazine and 9-ethylcarbazole are given. All the compounds (**4** - **6**) exhibit a broad absorption with λ_{max} in the range of 210-390 nm and demonstrate the red shift of UV absorption with respect of 10-alkylphenothiazine or 9-alkylcarbazole, respectively. This observation shows that the molecules synthesized are conjugated through the ethylene moiety and heterocyclic units and that π-electrons are de-localised over these molecules. The extended conjugation stabilizes the oxidized state of molecules and the diarylethylenes are expected to demonstrate lower values of ionization potentials (I_p) than compounds with electronically isolated phenothiazine or carbazole rings.
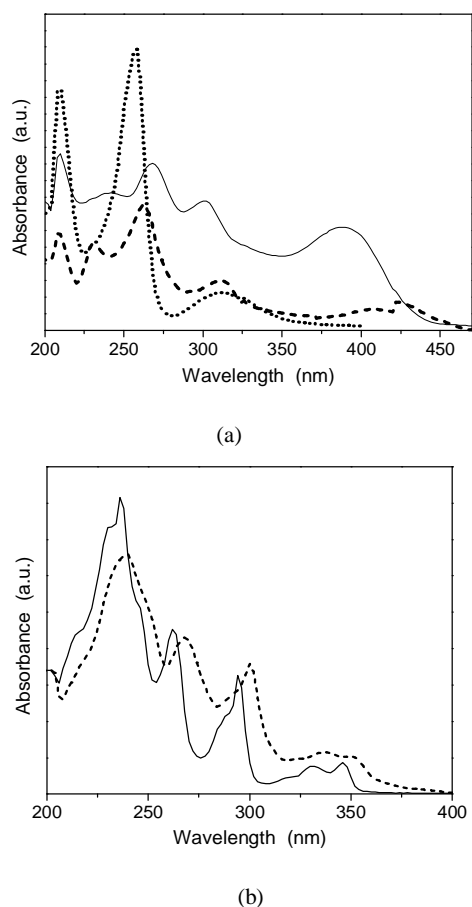

(a)

(b)

Fig. 2. UV absorption spectra of dilute solutions (a) of 4 (dashed line) and 5 (solid line) with 10-(2-ethylhexyl) phenothiazine (dotted line), and (b) of 6 (dotted line) with 9-ethylcarbazole (solid line).

Fig. 3 shows the fluorescence excitation and emission spectra of THF solutions of compounds **5** and **6**. The spectral profiles of **5** and **6** were found to be invariant with the excitation wavelength (for emission spectra) and emission wavelength (for excitation spectra). Similar emission spectra were obtained at a range of different excitation wavelengths (300, 340, 370, 390 nm) for both compounds. The excitation spectrum of **5** showed a broad band ranging from 210 to 460 nm with λ_{max} at around 392 nm. The solution emitted in the bluish-green region with a maximum at 495 nm. The emission band was very broad and without any vibrational structure. The breadth of the absorption (excitation) and emission bands can be attributed to the decreased planarity of the molecules caused by the large steric interactions within the molecule. A relatively large Stokes shift of 105 nm was observed. This shift can be attributed to changes in the molecular structure of the phenothiazine moieties upon excitation, in which the difference in energy between the geometrically relaxed ground state and the non-relaxed excited singlet state is larger than the energy difference between the geometrically relaxed excited state and the non-relaxed ground state [21]. Additionally, the fluorescence spectrum of **5** is red shifted (~40 nm) when compared to those of 10-alkylphenothiazines obtained under the same conditions [22]. This shift could be due to a different rearrangement of solvent molecules in the transient ground state and singlet-excited state, because of the presence of an extra phenothiazine moiety.
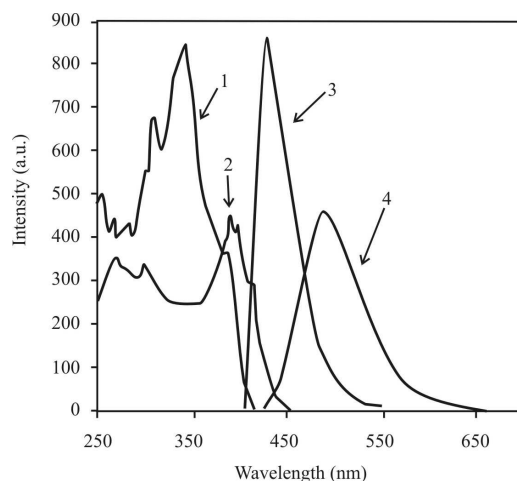

Fig. 3. Steady-state fluorescence spectra (normalized to common maximum intensity) of 5 and 6 in THF (10^{-5} M). The excitation spectra were measured at 430 nm for 6 (1) and at 490 nm for 5 (2). The fluorescence emission spectra were obtained with λ_{ex}= 340 nm for 6 (3) and λ_{ex}= 390 nm for 5 (4).

The excitation spectrum of **6** shows a broad band ranging from 210 to 390 nm with two characteristic bands at around 310 nm and 340 nm. The emission spectrum of **6** indicates complete absence of emission from 'monomeric' or unassociated excited state of carbazole moiety. The obtained emission spectrum was completely different compared to that of the model compound 9-ethylcarbazole.

The fluorescence spectrum of **6** has a featureless blue emission band centred at 433 nm resulting in a Stokes shift of 90 nm.

Fluorescence quantum efficiency of the THF solutions of 1,2-diarylethylenes **4, 5** and **6** was estimated to be 28 %, 20 % and 13 %, respectively, as determined by comparison with standard of known quantum yield. Moderate quantum efficiencies revealed are consistent with the large Stokes shift (~100 nm) estimated in these compounds, which most likely increases contribution of nonradiative decay pathways in the recombination process.

Chromaticity coordinates (x,y) of the compounds **4 – 6** were evaluated on the basis of the trichromatic system of modern colorimetry developed by CIE in 1931. First, the tristimulus values X, Y, and Z representing the relative quantities of the primary colors were obtained by integrating the emission spectrum with the standard color-matching functions $\overline{x}(\lambda)$, $\overline{y}(\lambda)$, and $\overline{z}(\lambda)$ tabulated in Ref. [23]. Following the normalization procedure of the tristimulus values, the normalized color value components x and y i.e., chromaticity coordinates, were calculated. For detailed description of the evaluation procedure see Ref. [24]. Similar chromaticity coordinates of (0.20, 0.41) and (0.21, 0.43), which refer to the bluish-green part of the chromaticity diagram, were obtained for the compounds **4** and **5**, respectively. We note that the chromaticity coordinates of **6** [(0.16, 0.05)] were very close to those of the primary blue color [(0.15, 0.06)] used in the modern NTSC, PAL and SECAM systems. The use of **6** as the primary blue when developing new OLED displays could avoid inconsistencies with modern broadcasting standards caused by color mismatch.

The fluorescence decay dynamics of both compounds in dilute THF solution was examined by monitoring their photoluminescence maxima. The fluorescence decay curves of both molecules with the corresponding exponential fits are shown in Fig. 4, along with the decay parameters given in Table 2.
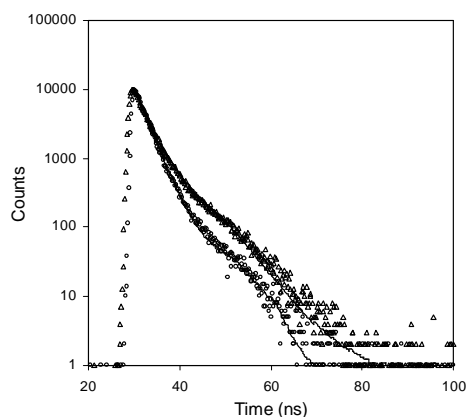

Fig. 4. Fluorescence decay curves of the dilute solutions of 5 and 6 in THF (10^{-5} M) with the excitation of 390 nm and 340 nm, respectively. Open symbols represent the actual data and the solid lines are fits to the data. The decay of 5 ($\circ$, λ_{em}=430 nm) fitted to a single-exponential model, the decay of 6 ($\triangle$, λ_{em}= 490 nm) fitted to a dual-exponential model.

The decay of the emission of **5** was independent of the excitation wavelength. All obtained fluorescence decay curves of the molecule were best described by a monoexponential decay function, giving a τ_f of 2.5-2.6 ns for the dilute solutions of **5** in THF. The observed lifetimes are within the range of values reported for 10-alkylated phenothiazine derivatives [25]. The fluorescence decay dynamics of **6** was not monoexponential, requiring two exponentials to achieve best fits of the data. Two components are present in the time-dependent fluorescence of the compound. The short-living component gave dominant fluorescence lifetimes of ~2 ns and longer living component gave the lifetimes in 3-7 ns range. All fluorescence decays obtained using different excitation wavelength show similar decay characteristics.

Table 2. Fluorescence decay parameters resultant upon single or double exponential fitting to the time-resolved fluorescence of compounds 5 and 6 in THF (c= 10^{-5} M).

Compound	λ_{ex}	λ_{em}	τ_1 (ns)	τ_2 (ns)	χ^2
5	300	490	2.63±0.01		2.20
	340	490	2.62±0.01		1.81
	375	490	2.55±0.01		1.79
	390	490	2.52±0.01		1.75
6	310	430	3.55±0.03		8.45
			2.59±0.05 (0.73)	6.88±0.10 (0.27)	1.74
	340	430	3.20±0.02		6.55
			2.30±0.04 (0.68)	5.60±0.11 (0.32)	2.52
	375	430	3.02±0.02		4.24
			2.24±0.04 (0.66)	4.82±0.10 (0.34)	2
	385	430	2.83±0.02		3.75
			0.21±0.01 (0.12)	2.87±0.02 (0.88)	3.48

Fig. 5 shows the normalized fluorescence excitation and emission spectra of the thin films of **5** and **6**. The thin film excitation spectrum of **5** is identical to the dilute THF solution spectrum. The thin film emission spectrum of **5** is nearly identical to that in dilute solution (see Fig. 3); the slight difference is that the broadening of the emission band of solid-state sample is evident. This correspondence of the fluorescence spectra of **5** in dilute solution and solid state clearly rules out intermolecular aggregates or excimers as the origin of emission in this compound. It is known that the phenothiazine ring is highly nonplanar in the ground state, precluding sufficiently close intermolecular interactions essential to forming aggregates or excimers [26].
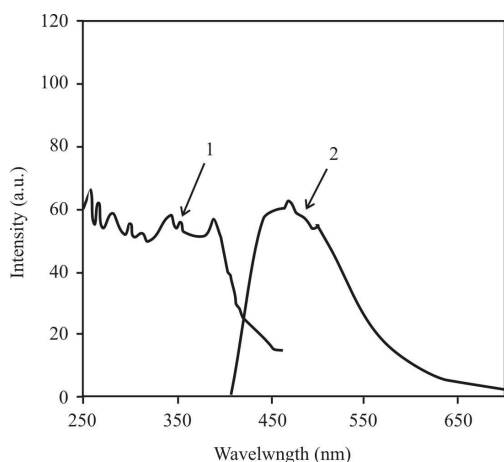
Fig. 5. Steady-state fluorescence spectra (normalized to common maximum intensity) of thin film of 5. The excitation spectra were measured at 500 nm for 5 (1). The fluorescence emission spectra were obtained with λ_{ex}=390 nm for 5 (2).

Fluorescence decays of the thin films of the synthesized compounds were generally difficult to measure by the instrument used as a result of the short lifetimes involved and very week intensity of the emission of the thin films. These measurements were further complicated by scattered excitation light. Attempts to completely eliminate light scattering contamination were unsuccessful. Contamination of the decays by scattered excitation can make the emission decay behaviour appear to be more complex than actuality. This was considered to be the major cause of the inability of single and double-exponential functions to provide adequate fits. The solid-state fluorescence decay dynamics of the compounds 5 are shown in Table 3.

Table 3. Fluorescence decay parameters resultant upon triple exponential fitting to the time-resolved fluorescence of thin films of compound 5 in air and nitrogen atmosphere.

Sample	λ_{ex}	λ_{em}	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	χ^2
Thin film of 5, N_2 atmosphere	370	500	0.17±0.01	0.42±0.01	2.50±0.08	6.71
Thin film of 5, air atmosphere	370	500	0.13±0.01	0.43±0.01	2.64±0.07	5.29

The analysis parameters show that in all cases fluorescence decay of the thin films of 5 cannot be described adequately even by triple exponential decay function. Similar results were produced analysing samples in air and nitrogen atmosphere. The short-lived emission is characteristic for compound 5 and τ_f values ≤ 3.5 ns were obtained. The low emission intensity of the thin films of this compund might be caused by some energy deactivation phenomena.

Electron photoemission spectra of the films of compounds 4 - 6 are presented in Fig. 6. The values of I_p

for the films of the materials range from 5.3 to 5.4 eV. As expected, I_p of the phenothiazinyl- or carbazolyl-based ethylenes are lower than that of derivatives having electronically isolated phenothiazine or carbazole rings (I_p ~ 5.7 - 5.8 eV) [ii,27]. Holes would be easily injected into the layers of these materials from a charge generation layer or a conductive anode with I_p or work function close to 5.3 eV. It should be mentioned that I_p values for charge generation materials, including those widely used in electrophotographic photoreceptors, e.g. pigments, such as titanyl phthalocyanines [28,29], perylene pigments [30] and bisazo pigments [31] are in the range of 5.1-5.6 eV. The I_p values of compounds 4 – 6 are close to that of indium-tin oxide (ITO) which is widely used as an anode in electroluminescent devices [32]. The injection barrier of holes from the electrode into the layers of the materials synthesized would be 0.4 - 0.5 eV.
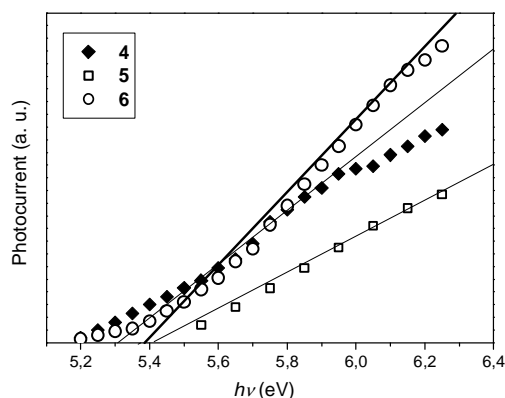

Fig. 6. Electron photoemission spectra of the compounds 4 - 6.

Compound 5 having the best solubility in organic solvents was used for charge carrier mobility studies. Time of flight measurements were used to characterise the magnitude of the hole drift mobility (μ_h) for the material molecularly dispersed in polymer host bisphenol Z polycarbonate (PC-Z). Electric field dependence of hole drift mobility for the solid solution of 5 in bisphenol Z polycarbonate is shown in Fig. 7.
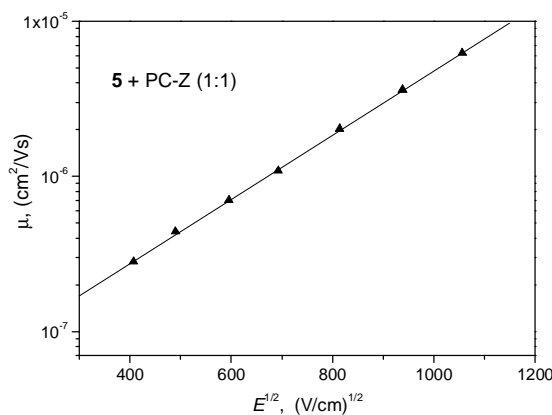

Fig. 7. The electric field dependence of hole drift mobility in charge transport layer of compound 5 doped in PC-Z (50 %).

The room temperature μ_h showed a linear dependence on the square root of the electric field. Such dependence is observed for the majority of non-crystalline organic systems and can be attributed to the effects of disorder on charge transport [33]. The solid solution of **5** in PC-Z (50 %) demonstrated hole drift mobility values reaching 8×10^{-6} cm^2/Vs at an electric field of 1.2×10^6 V/cm at room temperature.

4. Conclusions

We have synthesized thermally stabile phenothiazinyl- and carbazolyl-substituted ethylenes forming amorphous films and featuring emission in the green-blue spectral range with efficiency ranging from 13 % to 28 %. The dilute solutions of the compounds exhibited the dominant luminescence component decaying in ~2.5 ns and considerably shorter one in the thin films. Photophysical properties of the derivatives in solutions and in films were found to depend strongly on the aryl substituent at ethylene linkage. Electron photoemission spectra of the materials have been recorded and the ionisation potentials of 5.3-5.4 eV have been established. Room temperature hole drift mobility of the phenothiazinyl-based ethylene dispersed in polymeric host approached 8×10^{-6} cm^2/Vs at high electric fields.

Acknowledgements

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