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The synthesis and luminescence of π-conjugated polymers derived from 3,3′-dicarbazoles

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Abstract

Novel, soluble, π-conjugated copolymers comprising 3,3′-bicarbazole and phenylene or thieno[3,2-*b*]thiophene comonomer were synthesized using the palladium-catalyzed Heck reaction. The resulting copolymers exhibited good solubility in common organic solvents such as chloroform, chlorobenzene, etc. and good thermal stability. The photoluminescence spectral maxima of the polymers were located at 426 (sh. 454) and 479 nm, indicating that they were blue and greenish-blue emitting materials in solution, respectively. The HOMO levels of the polymers were −5.16 and −5.24 eV and the band gaps were 2.50 and 2.26 eV, respectively.
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1. Introduction

For the past decade, many classes of π-conjugated polymers have been synthesized and investigated in opto-electronic devices. Among this poly(*p*-phenylenevinylene)s (PPVs) and its derivatives are still the most popular materials used in light-emitting diodes (LEDs). The most commonly used comonomers in PPV derivatives are thiophene, fluorene, benzothiadiazole and carbazole derivatives. Carbazole-containing polymers, especially those with carbazole as the homopolymers or copolymers, have been extensively investigated due to their good hole transport and photorefractivity [1,2]. Moreover, carbazole derivatives are used as light-emitting layers [3–6] and organic field effect transistors [7] because they are photostable and show blue photo- and electroluminescence due to their relatively low-lying HOMOs and the large band gaps.

Among the vast array of known π-conjugated polymers, conjugated polyfluorenes (PFs) are the most promising candidates as blue-light-emitting polymers because of their highly efficient photoluminescence, excellent thermal and oxidative stabilities. However, PFs have a HOMO level at about −5.8 eV, and consequently, a large barrier for injection of holes from PEDOT, which translates into a low luminance. Therefore, PFs require additional hole-transporting layers to obtain efficient hole injection in EL devices [8,9].

Recently, some researchers reported luminescence properties of polymers that have carbazole moieties in the main chain [3]. Among the carbazole derivatives, a carbazolic dimer, i.e. bicarbazolylene has emerged as a promising class of luminescent materials, which can be utilized as the blue-light-emitting active layers.

By considering all these points we report here the first syntheses of two bicarbazolylene-containing polymers through the use of Heck reaction and some preliminary studies of their physical properties.

2. Experimental

2.1. Materials

Solvents purchased from TCI were used as-received unless stated otherwise. Tetrahydrofuran (THF) was dried over

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sodium and distilled. *N*,*N*-Dimethylformamide (DMF) and methylene chloride were dried over calcium hydride and distilled. Chemicals obtained from Aldrich or TCI were used as-received. All reactions were performed under nitrogen.

2.2. Instrumentation

Chemical structures of the compounds were characterized by ^{1}H NMR spectrometry (Varian, INOVA, 400 MHz) and FT-IR spectrometry (Perkin–Elmer, Paragon 500). The absorption maximum (λ_{max}) of polymer in tetrahydrofuran (THF) solution was recorded in Duksan Mechasys, Optizen III. The PL spectra of the polymers were obtained using a Perkin–Elmer Paragon 500 luminescence spectrometer. Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer DSC7 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The molecular weight and polydispersity were determined in THF solvent by a Waters GPC-410 calibrated with polystyrene standards.

2.3. Synthesis of 3,3′-bi(9-(2-ethylhexyl)carbazole) (**1**)

The solution of 5 g (17.9 mmol) of 9-(2-ethylhexyl)carbazole [10] in 10 ml of methylene chloride was added to the solution of 8.71 g (53.7 mmol) of $FeCl_3$ in 40 ml of methylene chloride. This mixture was stirred for 18 h at room temperature, and then filtered and washed with chloroform. The mixtures were stirred in water/ammonia mixture (60 ml/30 ml (28%)) for 0.5 h and then extracted with methylene chloride. The extract was dried over Na_2SO_4 and the solvent was evaporated. The mixture was purified by column chromatography (SiO_2, hexane/ethyl acetate = 98/2) and 89% of product was obtained as colorless oils. ^{1}H NMR ($CDCl_3$, ppm) δ 0.94 (m, 12H), 1.40 (m, 16H), 2.11 (m, 2H), 4.23 (m, 4H), 7.10–8.52 (m, 14H).

2.4. Synthesis of 3,3′-bi(9-(2-ethylhexyl)carbazole-6-carbaldehyde) (**2**)

The solution of 3 g (53.9 mmol) of **1** in 5 ml of fresh distilled dichloroethane was added dropwise to a mixture of 8.26 ml (538.8 mmol) of $POCl_3$ and 8 ml of DMF at 0 °C under nitrogen atmosphere. This mixture was let to warm up to room temperature slowly and then stirred at 80 °C for 7 h. The reaction mixture was cooled to 25 °C and extracted with dichloroethane. The product was purified by column chromatography (SiO_2, $CHCl_3$/hexane = 6/4) and 76% of product was obtained as a yellow solid. ^{1}H NMR ($CDCl_3$, ppm) δ 0.83 (t, 6H), 0.92 (t, 6H), 1.20–1.49 (m, 16H), 2.04–2.18 (m, 2H), 4.22 (d, 4H), 7.50 (m, 4H), 7.89 (d, 2H), 8.03 (d, 2H), 8.44 (s, 2H), 8.68 (s, 2H), 10.10 (s, 2H).

2.5. Synthesis of 9-(2-ethylhexyl)-3-(9-(2-ethylhexyl)-6-carboxaldehyde-9H-carbazole-3-yl)-6-9-(2-ethylhexyl)-3-(9-(2-ethylhexyl)-6-vinly-9H-carbazole-3-yl)-6-vinyl-9H-carbazole (**3**)

A solution of 2.64 g (65.2 mmol) of methyltriphenylphosphonium iodide in 100 ml of dried THF was treated with 2.1 equiv. of *n*-butyllithium at 0 °C. After stirring for 30 min, 2 g (32.6 mmol) of **2** was slowly added to the mixture, stirred at 0 °C for 1 h, and then at room temperature for 12 h. After completion of the reaction, the mixture was poured onto crushed ice (300 g) and extracted with methylene chloride and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography (neutral alumina oxide, hexane/methylene chloride = 6/4). As a result, 64% of product was obtained as the colorless oil. ^{1}H NMR ($CDCl_3$, ppm) δ 0.78 (m, 12H), 0.86 (m, 16H), 2.01 (m, 2H), 4.25 (m, 4H), 5.17 (d, 1H), 5.83 (d, 1H), 6.88 (q, 1H), 7.14 (m, 2H), 7.23 (m, 2H), 7.50 (d, 2H), 7.60 (d, 2H), 7.87 (d, 2H), 8.38 (s, 1H), 8.59 (s, 1H).

2.6. Synthesis of 2,5-dibromothieno[3,2-b]thiophene (**4**)

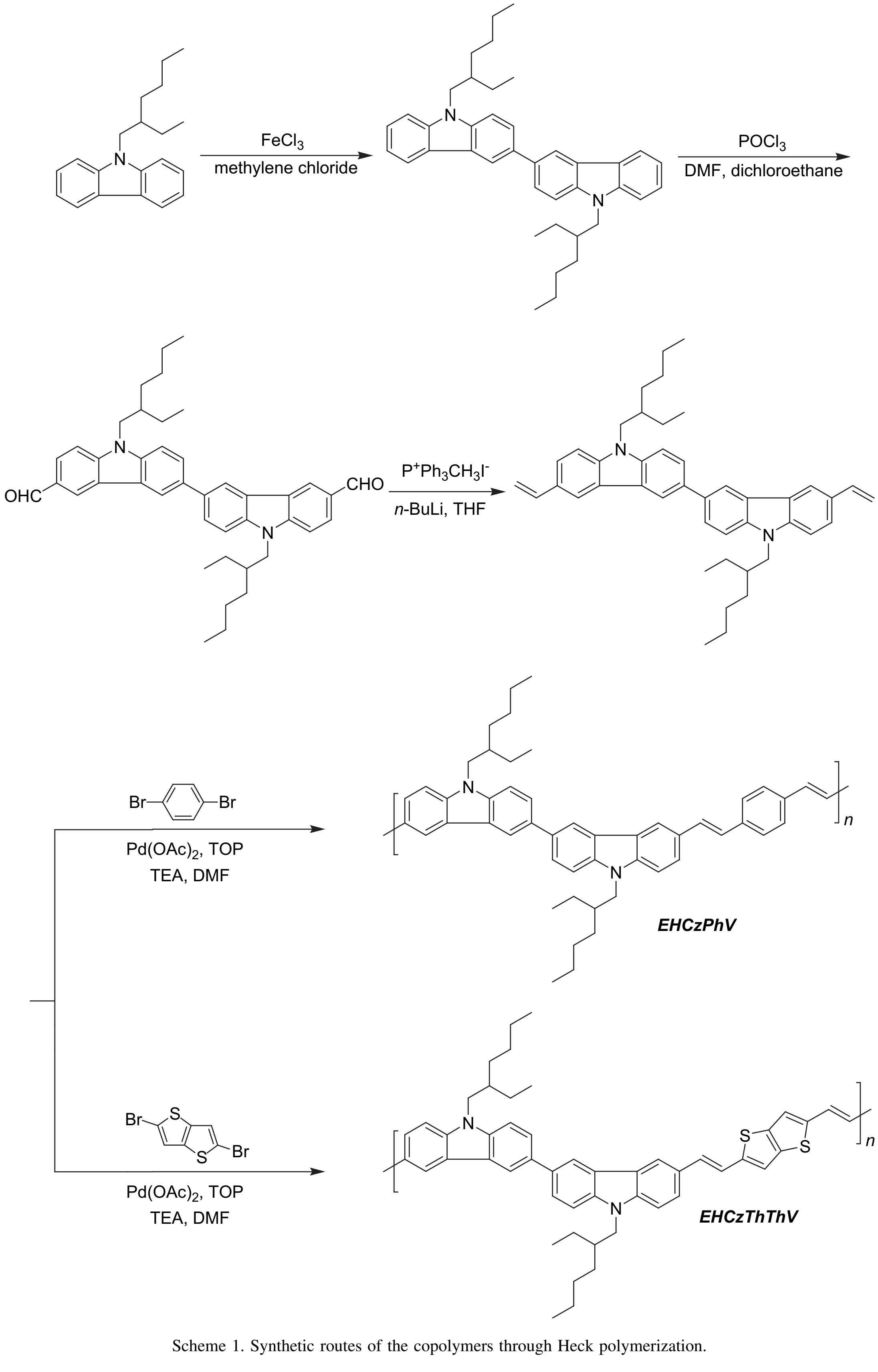
Thieno[3,5-*b*]thiophene was synthesized from 3-bromothiophene as indicated in Ref. [11]. A solution of 5.1 g (28.5 mmol) of NBS in 150 ml of DMF was added to a stirred and ice-cooled solution of 2 g (14.3 mmol) of thieno[3,2-*b*]thiophene in 10 ml of DMF. After the mixture was stirred for 3 h under ice cooling, crushed ice was added and the resulting mixture was extracted with methylene chloride. The extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to aluminum oxide column chromatography and 93% of product was obtained as the white solid. ^{1}H NMR ($CDCl_3$, ppm) δ 7.62 (s, 2H). IR (KBr pellet, cm^{-1}): 1014 (ν_{C-Br}).

2.7. General polymerization by the Heck reaction (**5**)

The synthesis of 3,3′-dicarbazole-based copolymers was carried out using well-known *Heck reaction* between divinyl-3,3′-dicarbazole monomers and aromatic or heteroaromatic dibromides, as shown in Scheme 1. Dibromo compound (0.1 mol) was dissolved in 5 ml of dry DMF at 50 °C under a nitrogen atmosphere. $Pd(OAc)_2$ (0.0005 mol) and tris(*o*-tolyl)phosphine (TOP: 0.045 mol) were added, dissolved, and stirred for 1 h. 3,3′-Dicarbazole moiety (0.1 mol) and triethylamine (TEA: 1.0 mol) were added, dissolved, and heated overnight to 110 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and poured into a large amount of methanol. The resulting precipitate was stirred for 1 h in methanol. The crude polymeric product was filtered off and dissolved in hot chloroform (100 ml). The solution was filtered through a glass filter to remove residual catalyst particles and precipitated in methanol. The precipitation process was continued until the polymer residue was free of monomers or the polymer was purified by Soxhlet extraction with methanol for 2 days. The obtained polymer was dried in a vacuum oven at 40 °C for 2 days.

2.7.1. Copoly[6,6′-bis(9-(2-ethylhexyl)carbazole-3-yl)/phenylenevinylene] (***EHCzPhV***)

The general procedure was followed using compound **3**, *p*-dibromobenzene, $Pd(OAc)_2$, TOP, TEA, and DMF at 110 °C for 24 h. The precipitate was collected by filtration and dried,



Scheme 1. Synthetic routes of the copolymers through Heck polymerization.

and then re-dissolved in $CHCl_3$, again precipitated in methanol followed by washing and drying. Yield: 54%. ^1H NMR ($CDCl_3$, ppm) δ 0.62–1.00 (br m, 12H), 1.03–1.64 (br m, 16H), 1.90–2.20 (br s, 2H), 3.95–4.30 (br s, 4H), 7.00–8.50 (br m, 20H).

2.7.2. *Copoly[6,6′-bis(9-(2-ethylhexyl)carbazole-3-yl)/thieno-(2,5-b)thiphenylidenevinylene]* (***EHCzThThV***)

The general procedure was followed using compound **3**, **4**, $Pd(OAc)_2$, TOP, TEA, and DMF at 110 °C for 24 h. The precipitate was collected by filtration and dried, and then re-dissolved in $CHCl_3$, again precipitated in methanol followed by washing and drying. Yield: 46%. ^1H NMR ($CDCl_3$, ppm) δ 0.70–1.04 (br m, 12H), 1.10–1.60 (br m, 16H), 1.98–2.20 (br s, 2H), 4.00–4.30 (br s, 4H), 7.05–8.44 (br m, 18H).

3. Results and discussion

The synthetic routes and structures of both the monomer and the resulting polymers are shown in Scheme 1. Compound **1** was synthesized by oxidative coupling of the corresponding monomers in the presence of a $FeCl_3$ catalyst in methylene chloride to afford 3,3′-dicarbazole in a high yield [12]. Compound **1** was used as a starting material for the preparation of **2** according to the Vilsmeier diformylation reaction, which was in turn converted to give the key intermediate, **3**, afforded by the well-known Wittig reaction between the dialdehyde and the methyltriphenylphosphonium iodide in the presence of *n*-butyllithium as a base. With a large excess of $POCl_3$/DMF (ca. 10 equiv), the diformylated **2** was produced with a good yield (76%). The absorption peaks of aldehyde C–H stretching of **2** were observed at 2830 and 2777 cm^{-1} and the characteristic C=O peaks for aldehyde groups were observed at 1643 cm^{-1} in IR spectrum. The chemical shifts of aldehyde proton were found at 10.10 ppm in ^1H NMR spectrum. After Wittig reaction, the ^1H spectrum of **3** shows that aldehyde proton peak of **2** at 10.10 ppm disappeared and new vinylic proton peaks appeared at 5.17, 5.83, and 6.88 ppm along with aromatic protons. The copolymers were synthesized via a Heck coupling reaction between **3** and **4** (or *p*-dibromobenzene). The Heck coupling was previously shown to have a great potential in polymerization reactions and leads to the formation of pure *trans* double bonds with very few side reactions. The ^1H NMR spectra of polymers exhibited broad resonance peaks typical of polymers. The starting vinylic proton peaks of **3** at ca. 5.17–6.88 ppm were completely disappeared when reaction times were over 24 h. The broad peak at around 3.95–4.30 ppm is assigned to the methylene protons adjacent to the nitrogen atom. Infrared spectra of polymer show a peak at 960 cm^{-1} that corresponds to the stretching of *trans*-vinylene bonds, whereas no peak corresponding to the stretching of *cis*-vinylene bonds can be seen in the 890–900 cm^{-1} region. This clearly confirms that only *trans* double bonds are formed by the Heck reaction. The synthesized polymers were soluble in common organic solvents such as chloroform, methylene chloride, THF, and DMF and it could be spin-cast onto glass plate to give highly transparent thin film. This is partially due to the 2-ethylhexyl side chain attached to the 3,3′-dicarbazole moiety.

In Table 1, the results for the polymerization were summarized. The yield of **EHCzPhV** and **EHCzThThV** is higher than 46% and the weight average molecular weight, M_w, of **EHCzPhV** and **EHCzThThV** determined by GPC *vs.* a polystyrene standard was 16 500 and 12 700 with a P.D.I (M_w/M_n) of 1.6 and 1.4, respectively.

The thermal properties of these polymers were studied using differential scanning calorimetry. The glass transition temperatures (T_g) of **EHCzPhV** and **EHCzThThV** copolymers were $T_g = 135$ and 112 °C, respectively. This results indicate that fused-thiophene group adjacent to the 3,3′-dicarbazole unit produces a little more rigid structure than the phenyl group due to steric hindrance between the vinyl linkage on a polymer backbone.

The UV–vis absorption spectra of the polymers were measured in THF (Fig. 1). The UV–vis spectrum of polymer solution exhibits broad absorption bands at 280–430 nm which are due to the carbazole and vinylic groups. The π–π^* transition peaks of **EHCzPhV** and **EHCzThThV** appear at 370 (304) and 365 nm (307 nm), respectively. The absorption maximum of the polymer solution occurred at 370 nm for **EHCzPhV** and 365 nm for **EHCzThThV**. These polymers present a broad and strong absorbance band like carbazole molecules in the UV–vis region. These polymers have a long tail band at above 450 nm, indicating the formation of intramolecular charge transfer complexes between the 3,3′-dicarbazole groups and the conjugated double bonds in the polymer backbone.

The photoluminescence (PL) spectra of the polymers are shown in Fig. 2. With an excitation wavelength of 370 nm, the **EHCzPhV** spectrum gives a peak in the emission spectrum at 426 nm, indicating a blue emission. In comparison the maximum in the PL spectrum of **EHCzThThV** is red-shifted to 479 nm, also showing blue emission. The edges of the absorption band of **EHCzPhV** and **EHCzThThV** are situated at 2.50 and 2.26 eV, respectively. The lack of mirror image relationship between the absorption and the emission spectra is related to the vibronic coupling [13]. The facts that the emission band is much narrow than the absorption bands and shows well-resolved vibronic bands are consistent with emission from localized excited states, most likely after a migration of the excitons along the polymer main chains to segments that represent low energy states. As expected **EHCzThTh** polymer exhibits slightly smaller red shift than **EHCzPhV** owing to the increased conjugation length of polymer backbone.

Table 1
Polymerization results of π-conjugated polymers

Polymer	Yield (%)	M_n[a]	M_w/M_n[a]	T_g[b] (°C)
EHCzPhV	54	16 500	1.6	135
EHCzThThV	46	12 700	1.4	112

[a] Determined by gel permeation chromatography based on polystyrene standards using THF as an eluent.

[b] Performed under a nitrogen atmosphere at a heating rate of 10 °C/min.

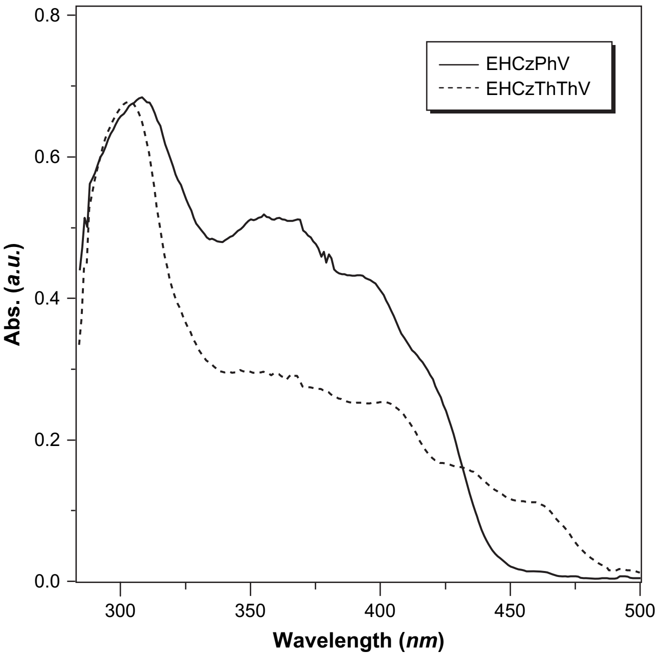


Fig. 1. UV–vis spectra of **EHCzPhV** and **EHCzThThV** solutions.

The Stokes shifts between the absorption and emission of these two polymers are relatively small, reflecting the rigid geometry of the conjugated main chain structures. The maximum of the absorption bands of **EHCzPhV** and **EHCzThThV** is almost the same. However, the PL spectra of these polymers are very different from that of the PL spectra exhibiting maximum emission bands. There are great differences between the Stokes shifts of the two polymers. **EHCzPhV** had a Stokes shift of 56 nm, which was almost twice that of **EHCzThThV**. Usually the Stokes shift comes from two sources: emission either from the excited segments of a conjugated polymer undergoing a deformation into more planar conformation along the chain or from the migrated excitons in other segments where ring rotations are not hindered [14,15]. It is expected that our designed polymer with phenylenevinylene unit (**EHCzPhV**) inserted into the polymer main chain had caused more rigid structures than **EHCzThThV** due to a much smaller Stokes shift.

The electrochemical properties of all polymers were investigated by cyclic voltammetry, as shown in Fig. 3. The polymers were coated onto a platinum electrode to form a thin

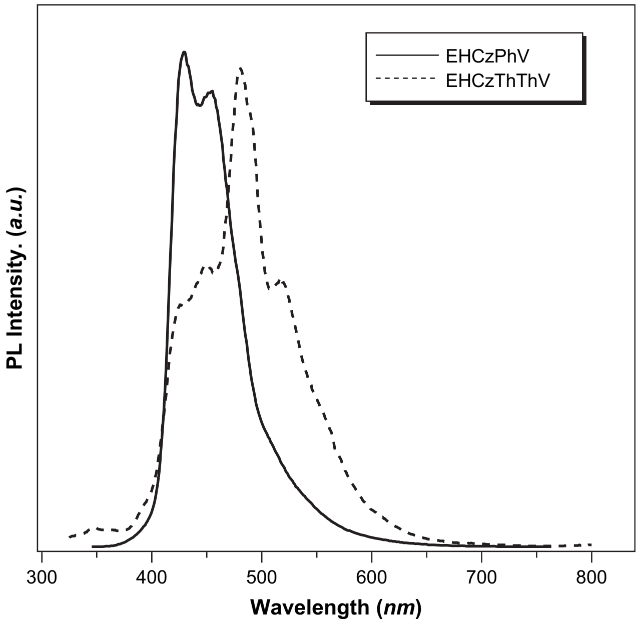


Fig. 2. PL spectra of **EHCzPhV** and **EHCzThThV** solutions.

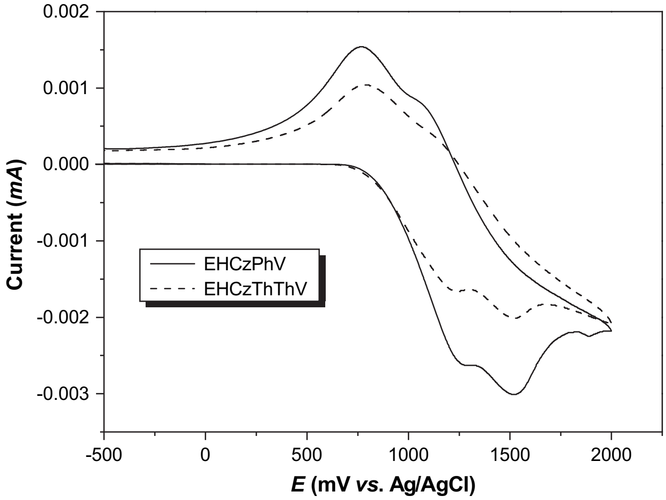


Fig. 3. Cyclic voltammograms of **EHCzPhV** and **EHCzThThV** films.

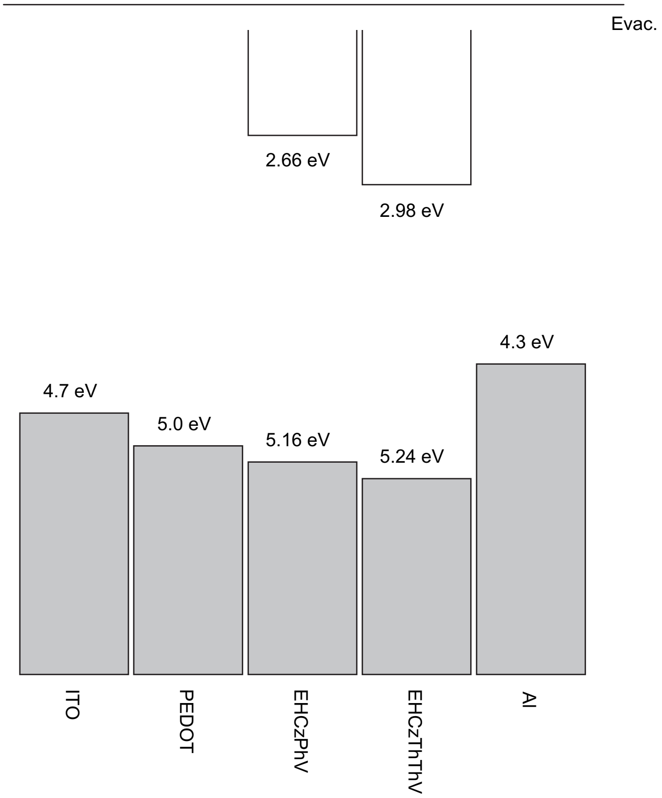


Fig. 4. Energy band diagram of PSX-DCZ and PSX-TPD.

Table 2
Optical and electrochemical properties of the polysiloxanes

Polymer	UV λ_{max}[a] (nm)	PL λ_{max}[b] (nm)	Band gap[c] (eV)	HOMO[d] (eV)	LUMO[e] (eV)
PSX-DCZ	304, 370	426	2.50	−5.16	−2.66
PSX-TPD	307, 365	479	2.26	−5.24	−2.98

[a] Maximum wavelength of absorption in THF.
[b] Maximum wavelength of photoluminescence in THF.
[c] Calculated from the absorption edge of the UV−vis spectrum.
[d] HOMO energy level was calculated by using ferrocence value of 4.8 eV below the vacuum level.
[e] Estimated from the HOMO and band gap.

film. This film was immersed in a 2 mM tetra-*n*-butyl-ammonium tetrafluoroborate acetonitrile solution. The potentials were recorded against an Ag/AgCl as reference electrode and each measurement was carried out using the ferrocence/ferrocenium (Fc) redox system as an internal standard. In anodic scan, the onset of oxidation for **EHCzPhV** and **EHCzThThV** occurred at 0.36 and 0.44 V (*vs.* SCE), which corresponds to the values of the ionization potential (IP) of −5.16 and −5.24 eV, respectively. The HOMO energy levels of these π-conjugated polymers greatly reduce the energy barrier for the hole injection from indium tin oxide (ITO) (4.80 eV) to the emissive Alq_3 (5.80 eV). The LUMO energy of the copolymers was estimated from the optical band gaps and the HOMO energies. Accordingly, the HOMO and LUMO energy levels of polymers **EHCzPhV** and **EHCzThThV** can be estimated as −2.66 and −2.98 eV, respectively (Fig. 4). The resulting data are also summarized in Table 2.

From CV measurements, the HOMO level of the 3,3′-dicarbazole copolymers is calculated to be at −5.16 to −5.24 eV. This means that the HOMO level of the 3,3′-dicarbazole copolymers is relatively close to the Fermi level of PEDOT:PSS (−4.9 eV), resulting in a good hole injection contact. The HOMO and LUMO of **EHCzThThV** are lower by 0.08 and 0.32 eV, respectively, than the HOMO and LUMO of **EHCzPhV**. Evidently, this is because of the extended π-conjugation extension of fused-thiophene unit in **EHCzThThV**.

4. Conclusion

We have successfully synthesized the new 3,3′-dicarbazole-based monomer and its copolymers with phenylene or theino [3,2-*b*]thiophene that show the possibility of blue emission. The photoluminescence (PL) spectral maxima of **EHCzPhV** and **EHCzThThV** were located at 426 (sh. 454) and 479 nm, indicating that they are blue and greenish-blue emitting materials in solution. As a result we confirmed that it is possible to use the new polymer as a good emission source for light EL device.

Acknowledgements

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