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Synthesis, optical and electrochemical properties of luminescent copolymers containing *N*-hexyl-3,8-iminodibenzyl chromophores

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Abstract

Novel copolymers carrying *N*-hexyl-3,8-iminodibenzyl chromophores have been synthesized by polycondenzation of *N*-hexyl-3,8-diformylminodibenzyl with 1,4-xylylene-bis(diethylphosphonate) via the Horner reaction (P1) or with 1,4-phenylenediacetonitrile via the Knoevenagel reaction (P2). The reduced viscosities of P1 and P2 are 1.17 and 0.43 dl/g, respectively. The P2 with electron-withdrawing CN groups can be dissolved in common organic solvents such as chloroform, THF, and toluene. Absorption, fluorescence, and cyclic voltammetric methods were employed to investigate their optical and electrochemical properties. The PL wavelength maxima of P1 and P2 are 494 (blue–green) and 542 nm (yellow–green), respectively. The oxidation potential of model *N*-hexyliminodibenzyl (1.33 V) is much smaller than that of conventional 9-hexylcarbazole (1.73 V), indicating iminodibenzyl is an effective chromophore in raising HOMO level. Comparing with P1 (HOMO: 4.96 eV, LUMO: 2.41 eV), incorporation of CN groups in P2 readily lowers the energy levels of HOMO (5.15 eV) and LUMO (2.84 eV). The energy barrier between aluminum cathode ($\Phi = 4.3$ eV) and P2 is narrowed significantly so that improved charge injection can be attained.

Keywords: Iminodibenzyl; Photoluminescence; Cyclic voltammetry

1. Introduction

Conjugated polymers, represented by poly(*p*-phenylene vinylene) (PPV) derivatives, have attracted much attention because of their potential applications as electroluminescence (EL) materials for light-emitting diodes (LEDs) [1–6]. Since the first report of the PPV-based LEDs by the Cambridge group [7], a variety of conjugated polymers have been reported to exhibit EL [8–14]. However, the emission efficiency is still low due to imbalance in injection and transport between electrons and holes. At present, it is circumvented by multi-layer strategy, i.e. insertion of electron transport layer (ETL) and/or hole transport layer (HTL) between electrodes and emission layer. Most of the emission layers (EML) are vacuum-deposited low molar mass organic compounds or spin-coated polymers.

EL polymers containing aromatic carbazole [15,16], triphenylamine [17,18], or alkyldiphenylamine [19] chromophores were well known for their high hole transporting ability. Aromatic amino chromophores exhibited intense UV absorption spectra and had been used extensively as strong electron donors in the study of photoinduced energy transfer and electron transfer to electron acceptors [15,16]. PPVs containing triphenylamino or alkyldiphenylamino groups showed outstanding photoconductivity and were characterized as possessing a high charge carrier photogeneration efficiency ($\eta = 20\%$) [17–19] and lower threshold voltage when fabricated as emitting layer in LED device [18]. Iminodibenzyl is a diphenylamine wherein two *ortho* positions are joined by a dimethylene bridge. However, PPVs with iminodibenzyl chromophores have not been reported so far. In this work, two new copolymers with iminodibenzyl chromophores were prepared by different methods.

EL polymers such as PPV and their derivatives are basically emitting and hole-transporting materials, which have hole mobility, that is, orders of magnitude larger than electron mobility. They show relatively small barriers to hole injection from indium–tin oxide (ITO, $\Phi_a \sim 4.7$–4.8 eV) [12], and very large barriers to electron injection from air-stable cathodes such as aluminum ($\Phi_c \sim 4.0$–4.3 eV) [20]. The threshold voltages are usually higher for the LED device fabricated using these polymers. To reduce the operating voltages, Holmes et al. used Knoevenagel reaction to prepare poly(cyanoterephthalylidene) derivatives with a relatively strong electron withdrawing cyano group [21,22]. Comparing with PPV, these poly(cyanoterephthalylidene)s

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showed a relatively low threshold voltage and high quantum efficiency when fabricated as LED devices. This has been ascribed to the reduced energy barrier for electron injection, which results from the decreased energy level of LUMO caused by the introduction of electron-withdrawing CN groups.

In this work, we prepared two new copolymers containing alternate iminodibenzyl and distilbene (or cyanoterephthalylidene) chromophores in main chain. Their characterization, optical and electrochemical properties are investigated in detail.

2. Experimental section

2.1. Materials

Iminodibenzyl and 1-bromohexane were from TCI and Lancaster, respectively, and used without further purification. Lithium amide and phosphorus oxychloride were purchased from Aldrich Chemical Co. and used as received. *N*,*N*-Dimethylformamide (DMF) was purified by distillation over phosphorus pentoxide. 1,4-Phenylenediacetonitrile (99%), 1,4-xylylene-bis(diethylphosphonate) (95%) and sodium ethoxide (21 wt% solution in ethanol) were purchased from Aldrich, Fluka, and TCI, respectively, and used as received. All other solvents or chemicals were purified by the conventional method or used as received.

2.2. Measurements

FT-IR spectra were recorded on a Valor III spectrometer from Jasco. ^{1}H NMR spectra were recorded with a Bruker 400 MHz FT-NMR and chemical shifts were recorded in ppm using TMS as internal standard. Viscosities of polymers were measured at 30°C with a Ubbelohde viscometer in a solution of chloroform at a concentration of 0.15 g/dl. The thermogravimetric analysis (TGA) of the polymers was measured under nitrogen atmosphere at a heating rate of 20°C/min using a Perkin Elmer TGA-7 thermal analyzer. Absorption spectra of polymers were obtained using a Jasco V-550 spectrometer. Photoluminescence (PL) spectra were recorded using a Hitachi-4500 fluorescence spectrophotometer. Thin films used for the spectroscopic measurement were obtained by casting polymer solutions (3 mg/dl) onto quartz windows and drying successively at ambient temperature, 50°C, and in vacuo. The cyclic voltammograms (CV) of polymers were measured at room temperature under nitrogen atmosphere using polymer-coated ITO as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire electrode as auxiliary electrode supporting in 0.1 M (n-Bu)$_4$NClO$_4$/acetonitrile solvent.

2.3. Monomer synthesis

2.3.1. N-hexyliminodibenzyl (2)

To a two-necked flask containing iminodibenzyl (**1**: 2.013 g, 10 mmol), 1-bromohexane (1.852 g, 11.2 mmol) and 20 ml toluene were added portion wise with lithium amide (0.254 g, 10.5 mmol) at 60°C under stirring. The solution was allowed to reflux for 20 h and then washed with 150 ml water after cooling to ambient temperature. Evaporation of the solvent followed with purification by column chromatography (silica gel; hexane/ethyl acetate = 20/1) gave **2** as yellow oil (2.06 g, 74%). IR (KBr, cm^{-1}): 1326 (C–N), 825 (Ar-H). ^{1}H NMR ($CDCl_3$, ppm): δ 7.2 (m, 6H), 7.00 (d, J = 7.3 Hz, 2H), 3.82 (t, J = 7.0 Hz, 2H), 3.26 (s, 4H), 1.65 (quintet, J = 5.4 Hz, 2H), 1.39 (m, 2H), 1.33 (m, 4H), 0.95 (t, J = 3.3 Hz, 3H). Anal. calcd (%) for $C_{20}H_{25}N$: C, 86.02; H, 8.96; N, 5.02. Found: C, 85.86; H, 8.94; N, 5.02.

2.3.2. N-Hexylcarbazole

9-Hexylcarbazole has also been prepared for electrochemical investigation in comparison with *N*-hexyliminodibenzyl. It was synthesized by direct alkylation of carbazole reported previously [17]. To a 250-ml two-necked flask was added with carbazole (16.72 g, 100 mmol), 100 ml DMF, and potassium *tert*-butoxide (12.4 g, 110 mmol). After stirring for half-an-hour, the mixture was added with *N*-bromohexane (17.34 g, 105 mmol) and allowed to reflux overnight. Pouring it into a large amount of water precipitated 9-hexylcarbazole, which were collected by filtration and then recrystallized twice in methanol. The yield was 71% (mp: 53°C). IR (KBr, cm^{-1}): 1325 (C–N). ^{1}H NMR ($CDCl_3$, ppm): δ 8.13–8.10 (d, 2H), 7.50–7.40 (m, 4H), 7.26–7.21 (m, 2H), 4.31 (t, J = 7.0 Hz, 2H), 1.88 (quintet, J = 5.4 Hz, 2H), 1.39 (m, 2H), 1.31 (m, 4H), 0.88 (t, J = 3.3 Hz, 3H). Anal. calcd (%) for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.96; H, 8.40; N, 5.55.

2.3.3. N-hexyl-3,8-diformyliminodibenzyl (3)

To a two-necked 50-ml glass reactor containing phosphorus oxychloride (3.3 ml), were added *N*,*N*-dimethylformamide (5.8 ml) and *N*-hexyliminodibenzyl (**2**: 2.79 g, 10 mmol). The mixture was heated smoothly to 90°C and allowed to react for 20 h under stirring. It was then poured into a large amount of water, made basic (pH 12) using a 2N NaOH aqueous solution, extraction with chloroform. Removal of chloroform by a rotavapor resulted in crude brown oils. Purification by column chromatography (silica gel; hexane/ethyl acetate = 4/1) gave 1.8 g (54%) of **3** as light yellow oils. IR (KBr, cm^{-1}): 1690 (C=O) 1594, 1490 (aromatic C=C stretching), 1328 (C–N), 826 (Ar-H). ^{1}H NMR (acetone-d_6, ppm): δ 9.72 (s, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.48 (s, 2H), 7.09 (d, J = 7.3 Hz, 2H), 3.73 (t, 2H), 3.05 (s, 4H), 1.44 (quintet, J = 5.4 Hz, 2H), 1.16 (m, 2H), 1.07 (m, 4H), 0.68 (t, J = 3.3 Hz, 3H). Anal. calcd (%) for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.62; H, 7.58; N, 4.15.

Table 1
Preparation and solubility of P1 and P2 (+ + : soluble; + − : soluble on heating; − − : insoluble)

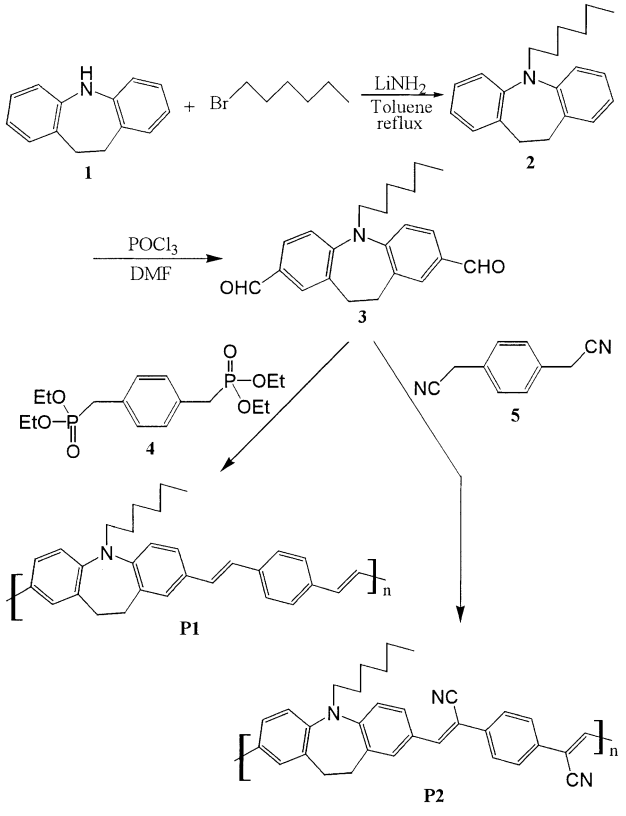
	Yield (%)	η_{red}[a] (dl/g)	T_d[b] (°C)	DMSO	DMAc	NMP	Pyridine	$CHCl_3$	THF	Toluene
P1	64	1.17	365	−	−	++	+−	++	+−	−
P2	65	0.43	293	++	++	++	++	++	++	++

[a] Reduced viscosity: 0.15 g/dl in chloroform at 30°C.
[b] Decomposition temperature at 5% weight loss measured by TGA under N_2 atmosphere.

2.4. Polymer synthesis

2.4.1. Poly(N-hexyl-3,8-iminodibenzyl-1,2-ethenylene-1,4-phenylene-1,2-ethenylene) (P1)

To a solution of 15 ml NMP and *N*-hexyl-3,8-diformyliminodibenzyl (**3**: 1.3 g, 3.43 mmol) was added with 1,4-xylylene-bis(diethylphosphonate) (**4**: 1.15 g, 3.43 mmol) and solid potassium *tert*-butoxide (0.898 g, 6.86 mmol). The mixture was stirred at ambient temperature for 10 h and then precipitated in a large amount of methanol to isolate solid products. The precipitation was repeated twice using chloroform as solvent to give bright yellow P1 (0.84 g, 64%). IR (KBr, cm^{-1}): 1594, 1490 (aromatic C=C stretching), 1324 (C–N), 814 (Ar-H). ^1H NMR ($CDCl_3$, ppm): δ 0.82–1.65 (m, 11H, aliphatic protons), 3.2 (4H, dibenzyl proton), 3.75 (2H, $-NCH_2-$), 6.95–7.45 (14H, aromatic and vinylic H). Anal. calcd for $C_{30}H_{31}N$. Found: $C_{29.6}H_{31}N_{0.95}$.



Scheme 1.

2.4.2. Poly(N-hexyl-3,8-iminodibenzyl cyanoterephthalylidene) (P2)

To a solution of *N*-hexyl-3,8-diformyliminodibenzyl (**3**: 0.335 g, 1 mmol) and 1,4-phenylenediacetonitrile (**5**: 0.158 g, 1 mmol) in 20 ml of anhydrous ethanol/chloroform (3/1) was added dropwise with a solution of sodium (0.648 g, 2 mmol) in 6 ml of anhydrous ethanol. The mixture was allowed to react for 5 h at ambient temperature, followed with precipitating in a large amount of ethanol to isolate solid products. The precipitation was repeated twice to give bright orange P2 (0.28 g, 65%). IR (KBr, cm^{-1}): 2210 (CN), 1589, 1492 (aromatic C=C stretching), 1330 (C–N), 836 (Ar-H). ^1H NMR ($CDCl_3$, ppm): δ 0.82–1.65 (m, 11H, aliphatic protons), 3.2 (4H, dibenzyl proton), 3.75 (2H, $-NCH_2-$), 6.95–7.45 (12H, aromatic and vinylic protons). Anal. calcd for $C_{32}H_{29}N_3$. Found: $C_{31.4}H_{29.1}N_{2.9}$ (see Scheme 1).

3. Results and discussion

3.1. Polymer preparation and characterization

The monomer *N*-hexyl-3,8-diformyliminodibenzyl (**3**) was synthesized by the well-known Vilsmeier reaction in a way similar to that reported by Choi Sam-Kwon et al. [16]. Then P1 was prepared by polycondensation of **3** with 1,4-xylylene-bis(diethylphosphonate) (**4**) via the Horner reaction. However, P2 was synthesized by the Knoevenagel reaction with 1,4-phenylenediacetonitrile (**5**). As summarized in Table 1, the yields are about 65% and the reduced viscosities (η_{red}) of P1 and P2 are 1.17 and 0.43 dl/g, respectively. The large difference in viscosity between P2 and P1 seems due to the much lower reactivity of corresponding 1,4-phenylenediacetonitrile than 1,4-xylylene-bis(diethylphosphonate). Moreover, P1 is soluble in common organic solvents such as NMP and $CHCl_3$. The solubility of P2 with cyano groups is much better than that of P1 and can be additionally dissolved in solvents such as THF, toluene, and pyridine. They could be spin-coated onto various substrates to give highly transparent and homogenous thin films. The decomposition temperatures of P1 and P2 were 365 and 293°C, respectively, as determined by TGA at 5 wt% loss. ^1H NMR and FT-IR spectra were employed to verify the structures of the polymers. For example, Fig. 1 shows the typical FT-IR spectra of P1 and P2 with that of starting dialdehyde monomer (**3**). The absorption peak of

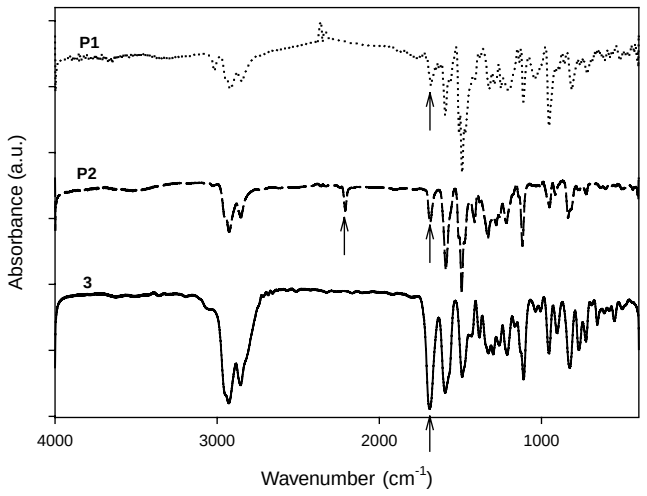


Fig. 1. FT-IR spectra of the dialdehyde monomer **3** (—), P1 (···) and P2 (- - -).

monomer **3** at 1682–1690 cm^{-1}, which is attributed to C=O stretching of aldehyde groups, decreases drastically in intensity when converted to polymers. On the other hand, there appears a sharp and a weak absorption peaks at 953 and

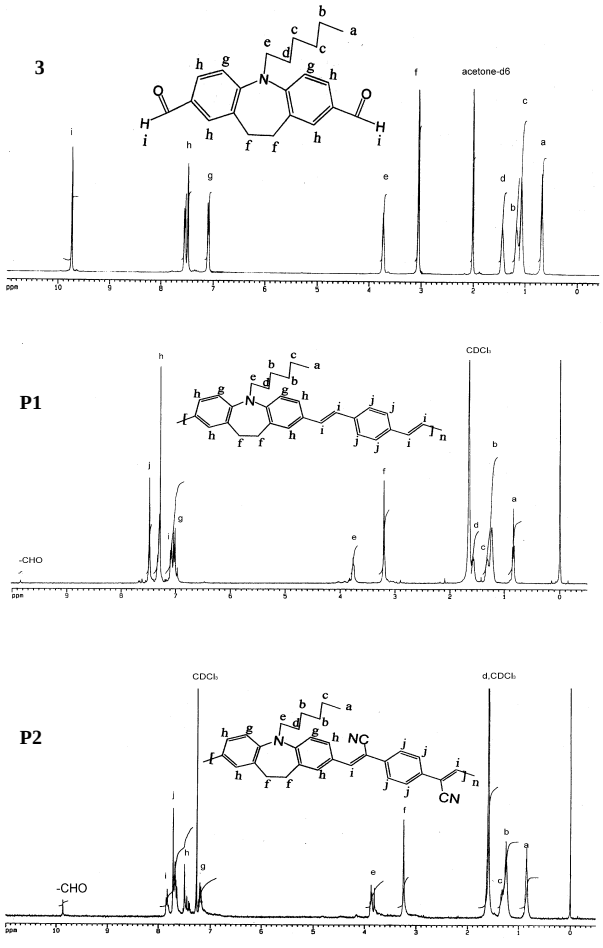


Fig. 2. ^{1}H NMR spectra (400 MHz) of **3**, P1 and P2.

Table 2
Absorption and photoluminescence maxima of P1 and P2 in solution and as films

Polymer	In solution[a]		As films		Stokes shift[b] (nm)
	UV (nm)	PL (nm)	UV (nm)	PL (nm)	
P1	408	474	419	494	75
P2	426	514	426	542	116

[a] In chloroform.
[b] Stokes shift (nm) = $PL_{(film)} - UV_{(film)}$.

946 cm^{-1} for P1 and P2 [9], respectively, which is corresponding to the out-of-plane bending mode of the *trans*-vinylene [16]. Moreover, the vibration absorption of CN groups in P2 can be clearly observed at 2210 cm^{-1}.

As shown in Fig. 2 for P1, the chemical shift of aldehyde protons at 9.82 ppm almost disappeared and new vinylic proton peaks appeared at about 7 ppm along with aromatic protons. The chemical shifts around 3.05 ppm were assigned to dimethylene bridge protons of iminodibenzyl chromophores, and the peak around 3.75 ppm is assigned to the methylene protons adjacent to nitrogen atom. For P2, the intensity of aldehyde peak at 9.87 ppm decreased significantly and new vinylic proton peaks appeared at 7.82 ppm along with aromatic protons. The assignments of other protons are similar to those in P1. However, for P2, the aldehyde proton peaks are greater than that of P1, indicating that the polymerization proceeds to a lesser extent. This is coincident with the much lower viscosity of P2 (0.43 dl/g) compared with that of P1 (1.17 dl/g).

3.2. Optical and photoluminescent properties

Figs. 3 and 4 show the absorption and photoluminescence (PL) spectra of P1 and P2 in solution and thin film states, respectively. Their absorption maxima and PL maxima were summarized in Table 2 for easiness of

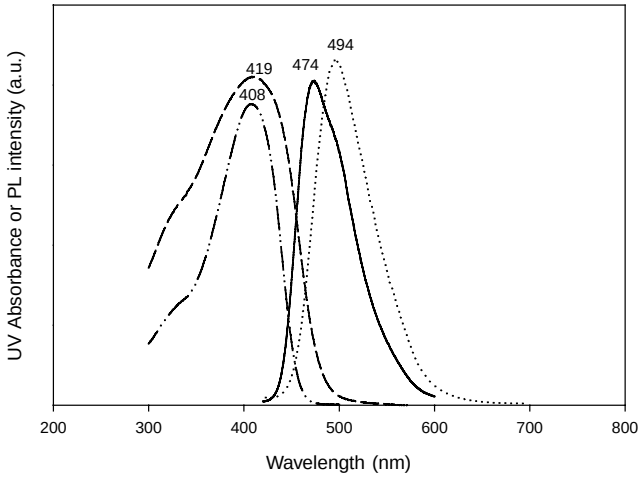


Fig. 3. Absorption spectra of P1 in solution (·· –) and as film (– – –), and PL spectra of P1 in solution (—) and as film (···).

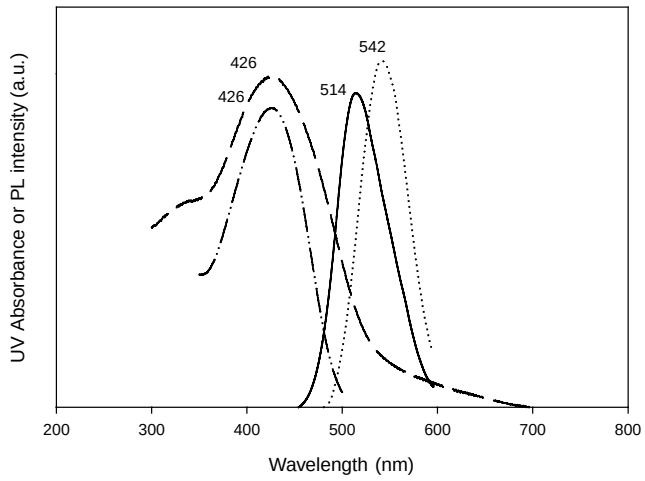


Fig. 4. Absorption spectra of P2 in solution (·· –) and as film (– – –), and PL spectra of P2 in solution (—) and as film (···).

comparison. The absorption maxima of P1 in solution and film states were located at 408 and 419 nm, respectively. These absorption peaks are mainly due to the $\pi-\pi^*$ transition of the π-conjugated distyrylbenzene segments in main chain. However, from the broad profile of absorption, it is considered that $\pi-\pi^*$ and/or $n-\pi^*$ transition of *N*-hexyl-3,8-diformyliminodibenzyl groups may also have contribution. For P2, the absorption maxima in both states shift bathochromically to 426 nm. The red shift can be attributable to the incorporation of electron-withdrawing CN group into the vinylene moiety in P2. The conjugation range and planarity are extended accordingly.

The photoluminescence maxima of P1 are located at 474 and 494 nm in solution and in thin film state, respectively. It exhibits conspicuous bathochromic shifts from 474 nm in chloroform solution to 494 nm in film state. Similarly, the PL maxima of P2 appeared at 514 nm in chloroform and 542 nm in film state. The bathochromic shifts of P1 and P2 in film state are 20 and 28 nm, respectively. Therefore, the interactions between polymer chains and chloroform are smaller than those among polymer chains in film state. Moreover, the wavelength of PL maxima in film state are much longer than that of absorption and the Stokes shift can be determined to be 75 nm for P1 and 115 nm for P2. It is noteworthy that in film state, the PL maximum of P1 (494 nm: blue–green) can be bathochromically shifted to 542 nm (yellow–green) in P2 by introducing cyano groups.

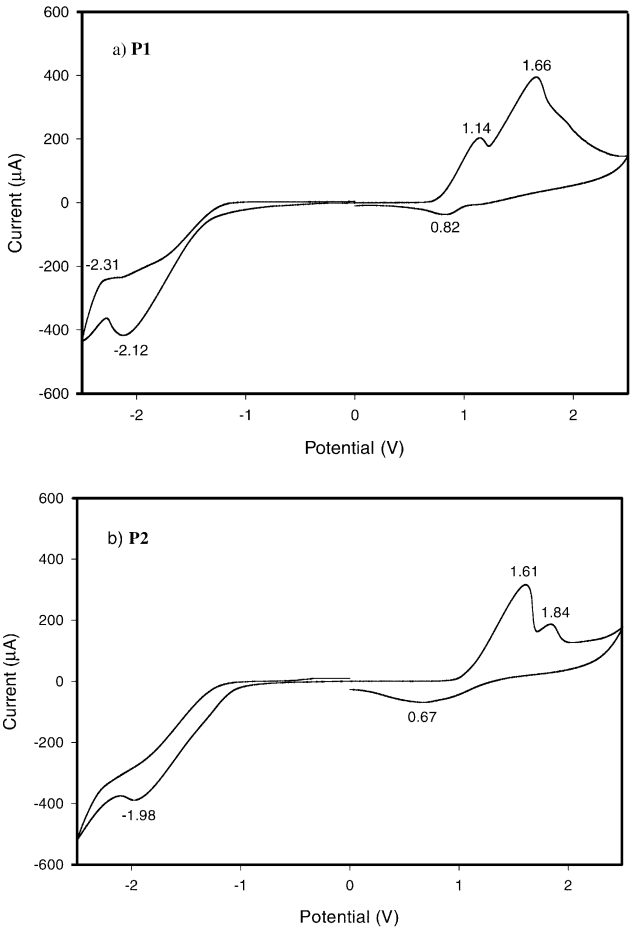


Fig. 5. Cyclic voltammograms of (a) P1 and (b) P2.

3.3. Electrochemical properties

The cyclic voltammograms, both anodic and cathodic directions of P1 and P2 between 2.5 and −2.5 V are shown in Fig. 5a,b. On sweeping P1 in anodic direction, two oxidation peaks at 1.14 and 1.66 V can be observed, which seem due to the first and second oxidation steps, respectively. However the reduction peak at about 0.82 V is not very clear, indicating that the electrochemical

Table 3
Optical and electrochemical properties of P1 and P2

Polymer	$E_{onset(ox)}$ vs. Ag/AgCl (V)	E_g^{opt} (eV)	$E_{onset(ox)}$ vs. E_{FOC}[a] (V)	HOMO (IP)[b] (eV)	LUMO (EA)[c] (eV)
P1	0.68	2.55	0.16	4.96	2.41
P2	0.87	2.31	0.35	5.15	2.84

[a] $E_{FOC} = 0.52$ V vs. Ag/AgCl.
[b] Ionization potential determined from the onset oxidation potential.
[c] Electron affinity determined from $E = IP - E_g^{opt}$.

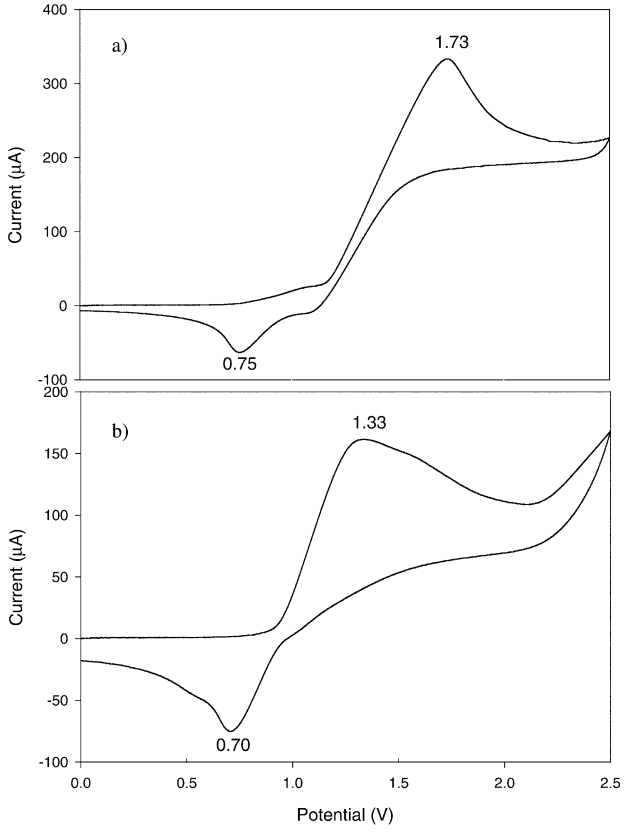


Fig. 6. Cyclic voltammograms of (a) *N*-hexylcarbazole and (b) *N*-hexyliminodibenzyl in 0.1 M $(n\text{-Bu})_4NClO_4$/acetonitrile solvent. Concentration: 0.001 M.

behavior in anodic direction is irreversible. For P2, two oxidation potentials in anodic direction appear at 1.61 and 1.84 V, which are greater than those of P1. This can be ascribed to electron-withdrawing cyano groups that enhanced electron affinity of emitting chromophores. A broad reduction peak locates at about 0.67 V, suggesting that similar to P1, the electrochemical behavior in anodic direction is also irreversible in P2. In cathodic scan, small oxidation peak at −2.12 V and reduction peak at −2.31 V can be observed for P1, but only oxidation one at −1.98 V for P2.

The band gap (E_g) of the polymers can be estimated from their absorption onset wavelength (UV_{onset}) [23,24]. In film state, the UV_{onset} of P1 and P2 are 487 and 536 nm, respectively, and the corresponding band gaps (E_g^{opt}) are 2.55 and 2.31 eV, respectively (Table 3). Moreover, the onset oxidation potentials ($E_{onset(ox)}$) can be estimated from anodic CV, in which the values are 0.68 and 0.87 V for P1 and P2, respectively. The positions of the HOMO (IP) and LUMO (EA) levels of P1 relative to vacuum can be estimated to be 4.96 eV ($IP = E_{onset(ox)} - E_{FOC} + 4.8 = 4.96$ eV) and 2.41 eV ($EA = IP - E_g^{opt} = 2.41$ eV), respectively. Similarly, the HOMO and LUMO levels of P2 are estimated to be 5.15 and 2.84 eV, respectively.

In order to elucidate the characteristic properties of

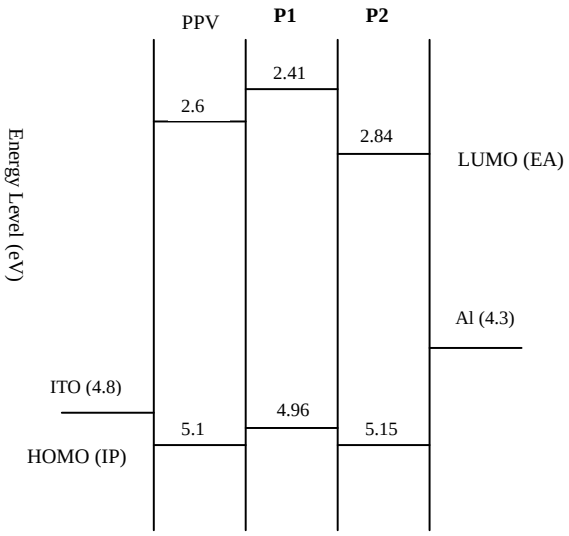


Fig. 7. Band diagrams of P1 and P2 determined from CV and UV/Vis spectroscopy.

the iminodibenzyl chromophore for electroluminescent application, electrochemical properties of the model *N*-hexyliminodibenzyl (**2**) and *N*-hexylcarbazole were also investigated. Fig. 6a,b depicts the CVs of *N*-hexylcarbazole and *N*-hexyliminodibenzyl, respectively, between 0 and 2.5 V. On sweeping *N*-hexylcarbazole in anodic direction, one significant oxidation peak appears at 1.73 V and reduction peak appears at about 0.75 V [25]. For *N*-hexyliminodibenzyl, the oxidation and reduction potentials appear at 1.33 and 0.7 V, respectively. Clearly, the oxidation potential of *N*-hexyliminodibenzyl is much lower than *N*-hexylcarbazole with similar reduction potentials around 0.7 V. This can be ascribed to relatively higher electron density on the nitrogen atoms of *N*-hexyliminodibenzyl, which in turn allows it to be more easily oxidized than carbazole derivatives [26,27]. Moreover, the charge of oxidized carbazole derivatives is not located on nitrogen atom but is delocalized over the entire molecule [26,27]. Therefore, incorporating iminodibenzyl chromophores to EL polymers should be helpful in raising HOMO level. This is ascertained by the fact that HOMO level of P1 (4.96 eV) is higher than those of PPV (5.1 eV) and P2 (5.15 eV) as shown in Fig. 7. However, electron-rich character of iminodibenzyl chromophores unavoidably results in higher LUMO level of P1 (lower electron affinity) [28].

The energy barrier (ΔE_e) between aluminum cathode (work function 4.3 eV) [29] and the LUMO of P2 (2.84 eV) is 1.46 eV and is significantly less than that of P1 ($\Delta E_e = 1.89$ eV). However, the energy barriers (ΔE_h) between ITO anode and polymers are just on the opposite and the ΔE_h values are 0.35 and 0.16 eV for P2 and P1, respectively. The change of the band gap due to derivation can be related to the electronic effects of the substituents on the HOMO and LUMO levels [30]. In our system, the effect

Table 4
Energy barrier between electrodes and polymers (P1 and P2)

Polymer	ΔE_h[a] (eV)	ΔE_e[b] (eV)	$\Delta E_e - \Delta E_h$[c] (eV)
P1	0.16	1.89	1.73
P2	0.35	1.46	1.11
PPV[d]	0.30	1.70	1.40

[a] Energy barrier between work function of ITO electrode and HOMO of polymers, $\Delta E_h = E_{HOMO} - 4.8$.
[b] Energy barrier between work function of aluminum electrode and LUMO polymers, $\Delta E_e = 4.3 - E_{LUMO}$.
[c] The difference of energy barriers between two electrode interfaces.
[d] Ref. [28].

of the cyano substituents is to lower both the LUMO and the HOMO levels [9].

Furthermore, energy difference between ΔE_e and anode ΔE_h can be employed to estimate the balance of charge injection. As shown in Table 4, the energy differences ($\Delta E_e - \Delta E_h$) of P1 and P2 are 1.73 and 1.11 eV, respectively, while that of PPV is 1.4 eV. Clearly, P2 with CN groups exhibits lower energy difference than PPV, indicating its enhanced balance in charge injection. However, the P1 shows greater energy difference than PPV mainly due to increased energy barrier (1.89 eV) with cathode. Therefore, P2 could be potentially applied to EL materials requiring balanced charge injection and transport.

4. Conclusions

Two new photoluminescent copolymers (P1, P2) containing *N*-hexyl-3,8-iminodibenzyl and divinylbenzene derivatives have been successfully prepared and characterized. The thermal decomposition temperatures of P1 and P2 are 365 and 293°C, and their viscosities are 1.17 and 0.43 dl/g, respectively. The P1 is soluble in NMP and $CHCl_3$, while for P2 with CN substituents, the solubility is significantly enhanced and can be additionally dissolved in DMSO, DMAc, pyridine, THF, and toluene. The PL wavelength maxima are located at 494 and 542 nm for P1 and P2, respectively. Iminodibenzyl chromophores are much more easily oxidized than widely used carbazoles. The HOMO and LUMO levels of P1 are estimated to be 4.96 and 2.41 eV, while those of P2 are 5.15 and 2.84 eV, respectively. In comparison with PPV, energy barrier between P2 and aluminum cathode is greatly reduced, while it remains almost unchanged between P2 and ITO anode.

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