Synthesis and photoluminescence properties of novel polyarylates bearing pendent naphthylamine chromophores

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ABSTRACT

A new series of blue photoluminescent aromatic polyesters (polyarylates) were synthesized from 1-[N,N-di(4-carboxyphenyl)amino]naphthalene with various bisphenols by the diphenylchlorophosphate (DPCP) activated direct polycondensation in a medium of pyridine and lithium chloride. The synthesis, basic characterizations, photoluminescence and electrochemical properties of this series of novel polyarylates bearing pendent naphthylamine chromophores were investigated. All polymers not only had good solubility in many polar aprotic solvents and excellent thin-film-forming ability, but also exhibited high T_g values, good thermal stability and lower highest occupied molecular orbital (HOMO) level. Thus, these naphthylamine-containing polyarylates may be widely applied in P-LED as hole-transporting layer and blue light-emitting materials due to their proper HOMO level, excellent thermal stability and fluorescence quantum efficiency.

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1. Introduction

It is well known that wholly aromatic polyesters (polyarylates) possess high thermal stability and excellent mechanical properties with high visible-light transparency [1]. The polyiso/terephthalate of bisphenol A (U-polymer) is an example of commercially available polyarylate that has a glass transition temperature (T_g) of 195 °C and is melt processable. Recently, modulation of their photophysical and electrical properties by means of a simple condensation synthetic method may be an impressive challenge in terms of new development of polymeric light-emitting diodes (PLEDs) materials.

Polymeric light-emitting diodes (PLEDs) are readily available in all the three primary colors. However, blue light-emitting materials remains an area of intense research activity to compete with the GaN-based inorganic LEDs. Furthermore, in full-color displays, the polymer with

a large energy band gap that can efficiently emit blue light and also serve as the energy-transfer donor in the presence of low energy fluorophores is highly desirable.

In order to obtain high-T_g's hole-transporting layer and blue light-emitting materials, many investigations have been done, such as triarylamine (TPA) and carbazole (Cz) based polymers used in multilayer organic electroluminescence (EL) devices [2–6], poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF) based polymers containing TPA or Cz in the emissive π-conjugated core/main chains [7–11] or grafting them as side chains in a polymer [12–14] or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges [15,16]. Recently, we also have reported the synthesis of organosoluble aromatic poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s bearing naphthylamine chromophore in the main chain based on 1-[N,N-di(4-carboxyphenyl)amino]naphthalene [17] with high quantum yield of 34% and 32% in N-methyl-2-pyrrolidone (NMP), respectively. And polyarylates bearing triphenylamine groups in the main chain based on 4,4′-dicarboxytriphenylamine

[18] with high quantum yield of 32.6% in tetrahydrofuran (THF). Because of the incorporation of bulky naphthylamine chromophores or triphenylamine groups along the polymer backbone, all the polymers were amorphous with high T_g and enhanced thermal stability, showed good solubility in many polar aprotic solvents and good film-forming capability.

Here a newly series of blue photoluminescence aromatic polyesters (polyarylates) were synthesized from 1-[N,N-di(4-carboxyphenyl)amino]naphthalene with various bisphenols by the diphenylchlorophosphate (DPCP) activated direct polycondensation in a medium of pyridine and lithium chloride. The 1-naphthylamine moieties are bulky and aromatic ones, so it is good for preserving the thermal stability of the polymers. When the 1-naphthylamine moieties are incorporated into the polymer backbone to form a triarylamine structure, it would generally disrupt the coplanarity of the aromatic unit to decrease stacking efficiency, then reduce interchain interactions and the between chains space will be improved. After that the polymer solubility will elevate at the same time. As for the ester group linkage, a kind of nonconjugated spacers, we expect it will conduce toward large band gap for blue light emission.

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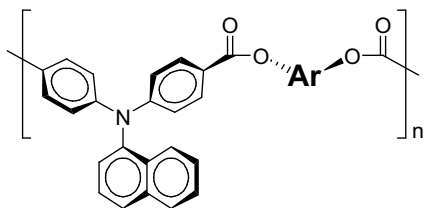
In addition, the prepared naphthylamine-containing polyarylates may find application in organic photoluminescent element because naphthylamine derivatives and polymers are reputed to be light-emitting materials and the ester group linkage will effectively prevent the electrons to delocalize along the polymer chains, so that the energy will not be quenched. The general properties such as solubility and thermal properties are reported, the electrochemical and photoluminescent properties of these polymers are also described herein and are compared with those of structurally related ones from 4,4′-dicarboxytriphenylamine (I′) [18].

2. Experimental

2.1. Materials

The naphthylamine-based aromatic dicarboxylic acid, 1-[N,N-di(4-carboxyphenyl)amino]naphthalene (2) (mp: 315–317 °C by differential scanning calorimetry, DSC), was successfully synthesized by the sodium hydride-mediated condensation of 1-aminonaphthalene with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dinitrile compound (1) (mp: 167–169 °C by DSC) according to a previously reported procedure [17]. 4,4′-Dicarboxytriphenylamine (mp: 313–315 °C by DSC) was synthesized by the condensation of aniline with 4-fluorobenzonitrile in the presence of sodium hydride, followed by the alkaline hydrolysis of the intermediate dinitrile com-

pound according to a previously reported procedure [19]. The bisphenol monomers that include 4,4′-dihydroxydiphenyl ether (3a) (TCI), 4,4′-isopropylidenediphenol (3b) (ACROS), 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (3c) (TCI), phenolphthalein (3d) (Aldrich), and 9,9-bis(4-hydroxyphenyl)fluorine (3e) (TCI) were purified by recrystallization from solvents. Commercially obtained anhydrous lithium chloride (LiCl) was dried under vacuum at 150 °C for 10 h. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice from ethyl acetate and then dried in vacuo prior to use. All other reagents were used as received from commercial sources.

2.2. Polymer synthesis

2.2.1. Preparation of the polyarylates via the direct polycondensation

The synthesis of polyarylate **Ib** was used as an example to illustrate the general synthetic route used to produce the polyarylates. A solution of diphenylchlorophosphate (DPCP) (0.69 g), LiCl (0.09 g), and pyridine (2.0 mL) was stirred at room temperature for 30 min and then added dropwise for 20 min to a hot solution (preheated at 120 °C for 5 min) containing 0.383 g (1.00 mmol) of 1-[N,N-di(4-carboxyphenyl)amino]naphthalene and 0.228 g (1.00 mmol) of 4,4′-isopropylidenediphenol (3b) in pyridine (2.0 mL). The final solution was heated with stirring at 120 °C for 3 h. The obtained polymer solution was poured slowly into 200 mL of stirred water giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by N,N-dimethylacetamide (DMAc)/methanol were carried out twice for further purification. These polymers collected by filtration and dried at 120 °C under vacuum. The inherent viscosity and weight-average molecular weights (M_w) of the obtained polyarylate **Ib** was 0.46 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C) and 28,500 daltons, respectively. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.71 (s, 6H, methyl), 7.10 (d, 4H, H$_j$), 7.17 (d, 4H, H$_b$), 7.28 (d, 4H, H$_k$), 7.43 (m, 2H, H$_c$ + H$_h$), 7.54 (t, 2H, H$_d$ + H$_g$), 7.83 (d, 1H, H$_i$), 7.91 (d, 1H, H$_e$), 7.96 (d, 1H, H$_f$), 8.06 (d, 4H, H$_a$). ^{13}C NMR (CDCl$_3$, δ, ppm): 30.9 (methyl), 42.5 (C^{19}), 120.9 (C^3), 121.1 (C^{16}) , 123.0 (C^1), 123.3 (C^{13}), 126.4 (C^7), 126.6 (C^{11}), 127.2 (C^{12}), 127.8 (C^6 + C^{17}), 128.2 (C^8), 128.7 (C^{10}), 130.8 (C^{14}), 131.7 (C^2), 135.3 (C^9), 141.4 (C^5), 147.8 (C^{18}), 148.8 (C^4), 151.5 (C^{15}), and 164.7 (ester carbonyl). The elemental analysis values of polyarylate **Ic** was calculated for (C$_{39}$H$_{23}$F$_6$NO$_4$)$_n$ (683.59)$_n$: C, 68.52%; H: 3.39%; N: 2.05%. Found for C, 68.50%; H, 3.95%; N, 2.01%. The other polyarylates (see Scheme 1) were synthesized by a similar procedure described as above.
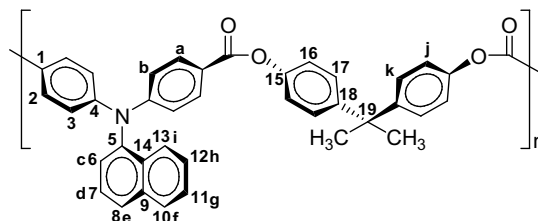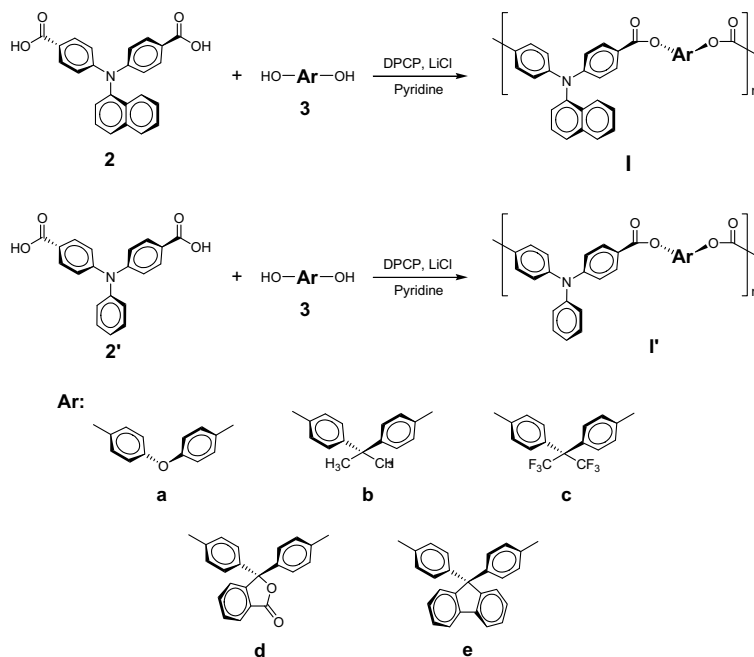
Scheme 1. Synthesis of aromatic polyarylates.

2.2.2. Preparation of the polyarylates films

A solution of polymer was made by dissolving about 0.5 g of the polyarylates sample in 8 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was heated at 80 °C for 1 h and 160 °C for 5 h to slowly release the solvent under vacuum. The obtained films were about 50–70 μm in thickness and were used for molecular weights measurements, solubility tests, thermal analyses, optical and electrochemical properties measurements.

2.3. Measurements

Infrared spectra were recorded on a Perkin–Elmer RXI FT-IR spectrometer. Elemental analyses were run in Vari-oEL-III Elementar. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a Varian Unity Inova 300 FT-NMR system and referenced to the CDCl$_3$ signal, and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (two column, MIXED-C and D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD Gmbh. All GPC analyses were performed using a polymer/THF solution at a flow rate of 1 mL/min at 40 °C and calibrated with polystyrene standards. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm^3/min). Thermomechanical analysis (TMA) was

conducted with a Perkin–Elmer TMA 7 instrument. The TMA experiments were conducted from 50 to 350 °C at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 50 mN. Softening temperatures (T_s) were taken as the onset temperatures of probe displacement on the TMA traces. Thermogravimentric analysis (TGA) was conducted with a Perkin–Elmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Absorption spectra were measured with a HP 8453 UV–visible spectrophotometer. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer. The fluorescence quantum yields (Φ_{PL}) of polymer solution were determined in THF against quinine sulfate (ACROS) in 1 N H$_2$SO$_{4(aq)}$ as the standard

Table 1
Inherent viscosity[a] and molecular weights[b] of polyarylates

Polymer	η_{inh} (dL/g)	M_w	M_n	PDI[c]	DP[d]
Ia	0.35 [0.41][e]	31,500	18,500	1.70	33.7
Ib	0.46 [0.25]	28,500	17,000	1.68	29.5
Ic	0.27 [0.27]	33,400	19,300	1.73	28.2
Id	0.25 [0.23]	31,800	18,800	1.69	28.2
Ie	0.31 [0.30]	28,300	16,800	1.68	24.1

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Calibrated with polystyrene standards, using THF as the eluent at a constant flow rate of 1 mL/min at 40 ºC.
[c] Polydispersity index (M_w/M_n).
[d] Degree of polymerization.
[e] Data in the parentheses are polyarylates I′ series.

(Φ_{PL} = 0.546) [20] were used. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. Electrochemistry was performed with a CHI 611B electrochemical analyzer. Cyclic
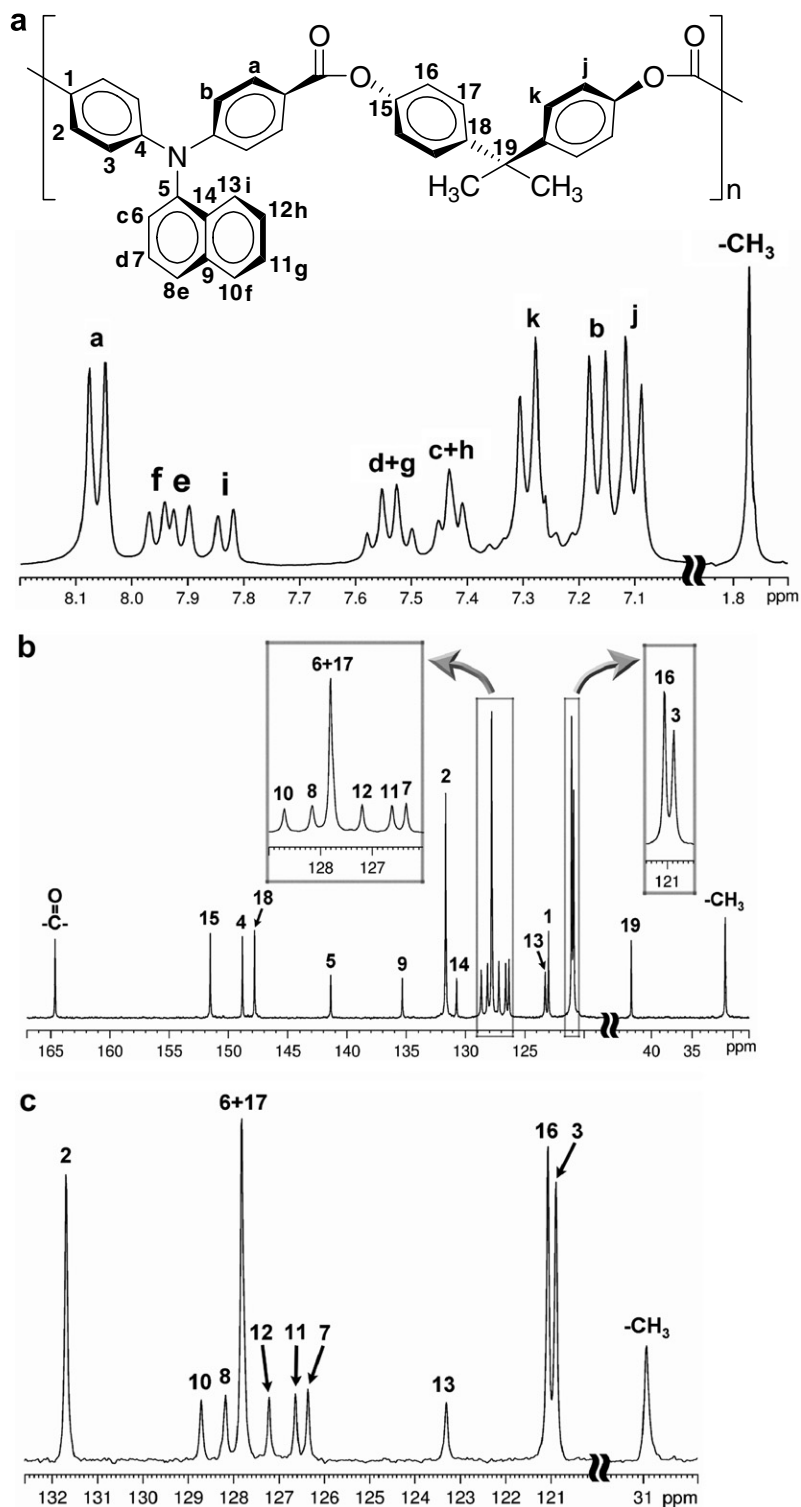

Fig. 1. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) DEPT-135 spectra of polyarylate **Ib** in CDCl$_3$.

voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.7 cm × 0.5 cm) was used as a working electrode and a platinum wire was used as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in solution of 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH$_3$CN). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. All cell potentials were taken with the use of a home-made Ag/AgCl, KCl (sat.) reference electrode.

3. Results and discussion

3.1. Polymer synthesis

A series of novel polyarylates with bulky pendent naphthylamine chromophores were prepared from the dicarboxylic acids, 1-[N,N-di(4-carboxyphenyl)amino]-naphthalene (2), and various aromatic diols (3) by the direct polycondensation reaction with DPCP and pyridine

as condensing agents [21] (Scheme 1). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, moderately high viscous polymer solutions. All of the polymers precipitated in a fiber-like form when the resulting polymer solutions were slowly poured into water. These polyarylates were obtained in almost quantitative yields with inherent viscosity values in the range of 0.25–0.46 dL/g (0.23–0.41 dL/g for series I′) and with weight-average molecular weights (M_w) and degree of polymerization (DP) in the range of 28,300–33,400 daltons and 24.1–33.7, respectively, relative to polystyrene standards (Table 1). The formation of polyarylates was confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. Most polyarylates could be solution-cast into good quality, transparent and colorless films. The structural feature of the polyarylates was confirmed by IR spectroscopy. The characteristic absorptions of ester group appear around 1735 cm^{-1} (C=O stretching) and in the region of 1200–1300 cm^{-1} (C–O stretching). Fig. 1 show a typical set of ^{1}H NMR, ^{13}C NMR and DEPT-135 spectra of polyarylate Ib in CDCl$_3$. The ^{13}C NMR spectras of
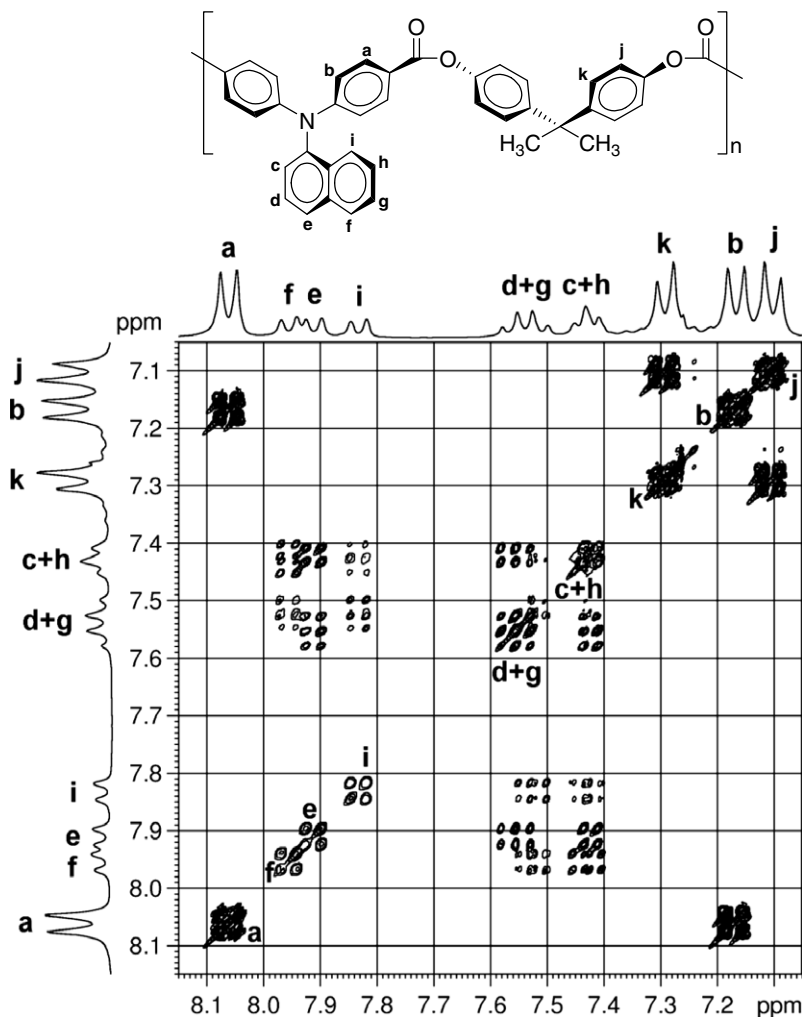

Fig. 2. H–H COSY (Correlation Spectroscopy) spectra of polyarylate Ib in CDCl$_3$.

polyarylate **Ib** confirmed that the signal at 164.7 ppm corresponding to the ester carbonyl carbon. All the ^{13}C atoms in polyarylate **Ib** resonated in the region of 120–155 ppm, and the singlet at 30.9 ppm due to the –CH$_3$ carbons. Assignments of each carbon and proton are assisted by the two-dimensional H–H COSY (correlation spectroscopy) and C–H HMQC (heteronuclear multiple quantum correlation) spectra shown in Figs. 2 and 3, and these spectra agree well with the proposed molecular structure of polyarylate **Ib**.
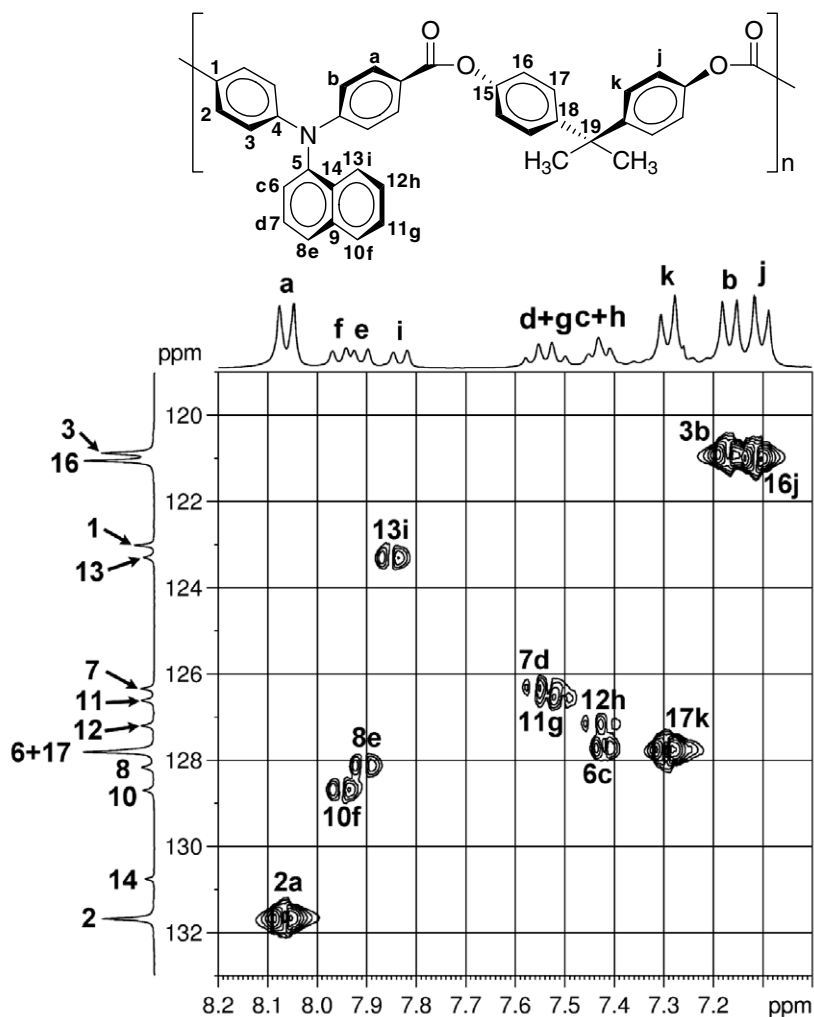

Fig. 3. C–H HMQC (Heteronuclear Multiple Quantum Correlation) spectra of polyarylate **Ib** in CDCl$_3$.

Table 2
Solubility[a] of polyarylates

Polymer code	Solvent							
	NMP	DMAc	DMF	m-Cresol	THF	CHCl$_3$	Toluene	CH$_3$CN
Ia	++	++	++	++	++	++	+	–
Ib	++	++	++	++	++	++	+	–
Ic	++	++	++	++	++	++	++	–
Id	++	++	++	++	++	++	+–	–
Ie	++	++	++	++	++	++	+	–
I′a	++	+	+–	+–	+	++	+–	–
I′b	++	++	++	+	++	++	++	–
I′c	++	++	++	+	++	++	++	–
I′d	++	++	++	+	++	++	+–	–
I′e	++	++	+–	+–	++	++	+–	–

++: soluble at room temperature; +: soluble on heating; +–: partial soluble or swelling on heating; –: insoluble even on heating.
  [a] The solubility was determined by using 1 mg sample in 1 mL of solvent.

3.2. Polymer properties

3.2.1. Basic characterizations

The solubility behavior of the polyarylates was tested qualitatively, and the results are summarized in Table 2. These high transparency polyarylates were very easily soluble in many common organic solvents such as NMP, DMAc, N,N-dimethylformamide (DMF), m-cresol, THF and chloroform ($CHCl_3$) and the solubility is somewhat much better than series **I′**. The solubility is really enhanced just like the aforementioned reason in the introduction. The more bulky pendent naphthylamine chromophores in the repeating unit surely play an important role to increase more free volume in the polymer chains so as to allow more solvent to come in. Thus, the excellent solubility makes these polymers convenient to processing into articles by spin- or dip-coating.

3.2.2. Thermal properties

The thermal properties of the polyarylates were investigated by DSC, TMA and TGA. The results are summarized in Table 3. The T_g of all the polyarylates could be easily measured in the DSC thermograms; they were observed in the range of 216–310 °C, depend on the structure of bisphenol components, and decreased with decreasing rigidity and symmetry of the polymer backbone. In addition, polymer **Id** and **Ie** containing a bulky group in bisphenol had the higher T_g value. All the polyarylates exhibited good thermal stability with insignificant weight loss up to 505 °C in nitrogen. The 10% weight-loss temperatures (T_d^{10}) of these polyarylates in nitrogen and air were recorded in the range of 520–555 and 505–535 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 50% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content.

Table 3
Thermal properties[a] of polyarylates

Polymer	T_g (°C)[b]	T_s (°C)[c]	T_d^5 (°C)[d]		T_d^{10} (°C)[e]		Char yield (wt%)[f]
			N_2	Air	N_2	Air	
Ia	216	216	520	495	540	510	57
Ib	248	243	515	475	535	505	50
Ic	239	240	505	490	525	505	57
Id	310	317	505	490	520	505	60
Ie	304	299	535	505	555	535	64
I′a	186	183	485	480	500	495	42
I′b	203	206	465	460	480	480	32
I′c	206	206	480	470	495	485	52
I′d	246	246	475	470	495	495	48
I′e	254	255	485	480	515	505	45

[a] The polymer film samples were heated at 200 °C for 1 h prior to all the thermal analyses.
[b] Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C/min) of the sample after quenching from 400 to 50 °C (rate: 200 °C/min) in nitrogen.
[c] Softening temperature measured by TMA with a constant applied load of 50 mN at a scan rate of 10 °C/min.
[d] Temperature at which 5% weight loss occurred, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 cm^3/min.
[e] Temperature at which 10% weight loss occurred.
[f] Residual weight percentage at 800 °C in nitrogen.

Table 4
Optical and electrochemical properties of polyarylates

Index	THF (1×10^{-5} M) solution, R.T.			Film (nm), R.T.				Oxidation/V[d]		E_g^f (eV)	E_{HOMO} (eV)[g]	E_{LUMO} (eV)
	λ_{max}	λ_{em}[a]	Φ_{PL} (%)[b]	λ_0[c]	λ_{max}	λ_{onset}	λ_{em}[a]	E_{onset}	$E_{1/2}$[e]			
Ia	355	428	28.1	390	357	390	448	1.31	1.36	3.18	5.67	2.49
Ib	354	426	34.9	390	354	392	448	1.31	1.36	3.16	5.67	2.51
Ic	357	437	30.4	385	358	392	446	1.30	1.36	3.16	5.66	2.50
Id	356	433	32.7	390	356	395	450	1.28	1.37	3.14	5.64	2.50
Ie	356	428	33.4	390	358	394	449	1.30	1.35	3.15	5.66	2.51
I′a	359	432	32.6	396	363	403	442	1.27	1.33	3.08	5.59	2.51
I′b	360	427	26.3	390	363	398	441	1.34	1.40	3.12	5.66	2.54
I′c	364	436	28.9	389	365	400	444	1.36	1.41	3.10	5.68	2.58
I′d	362	435	30.7	391	365	402	450	1.29	1.35	3.08	5.61	2.53
I′e	362	427	27.6	388	365	398	443	1.33	1.37	3.12	5.65	2.53

[a] They were excited at λ_{abs} for both solid and solution states.
[b] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of 10^{-5} M, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24–25 °C.
[c] The cutoff wavelength (λ_0) from the UV–vis transmission spectra of polymer films (thickness: 1–3 μm).
[d] vs. Ag/AgCl in $CH_3CN_{(1)}$.
[e] $E_{1/2}$ (average potential of the redox couple peaks).
[f] The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO).
[g] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

Comparing the thermal properties data of polyarylates **I** and **I′** in Table 3. One will find, that in series **I**, not only the T_g, T_s and T_d but also the char yield is superior than series **I′**. It means that the bulky naphthylamine chromophores are more effectively preserving the thermal stability in the prepared polyarylates.

3.2.3. Optical properties and electrochemical properties

The optical and electrochemical properties of the polyarylates were investigated by UV–vis and photoluminescence spectroscopy and cyclic voltammetry. The results are summarized in Table 4. These polymers exhibited strong UV–vis absorption bands at 354–357 nm in THF solution (Fig. 4), combine the $n-\pi^*$ transitions resulting from the conjugation between the aromatic rings and nitrogen atoms with the characteristic $\pi-\pi^*$ transitions of naphthalene chromophore (350 nm) [22]. The fluorescence spectra of the polyarylates in THF solutions (Conc.: 10^{-5} M)

exhibited emission maxima at 426–437 nm in the blue light region. The quantum yields of these polymers after refractive index correction can be calculated according to Eq. (1) [23]:

$$\phi_{unk} = \phi_{std} \left(\frac{I_{unk}}{I_{std}} \right) \left(\frac{A_{unk}}{A_{unk}} \right) \left(\frac{\eta_{unk}}{\eta_{std}} \right)^2, \tag{1}$$

where ψ_{unk}, ψ_{std}, I_{unk}, I_{std}, A_{unk}, A_{std}, η_{unk}, and η_{std} are the fluorescent quantum yield, integration of the emission intensity, absorbance at the excitation wavelength, and the refractive indices of the corresponding solutions for the samples and the standard, respectively. Here we use the refractive indices of the pure solvents as those of the solutions. The PL quantum yield in THF solution ranges from 28.1% for **Ia** to 34.9% for **Ib**. The fluorescence quantum yield (Φ_{PL}) of **Ib** (0.349) measured in THF is the highest among this series polymers. This may be the result of the lesser electron-withdrawing capability of methyl ($-CH_3$)
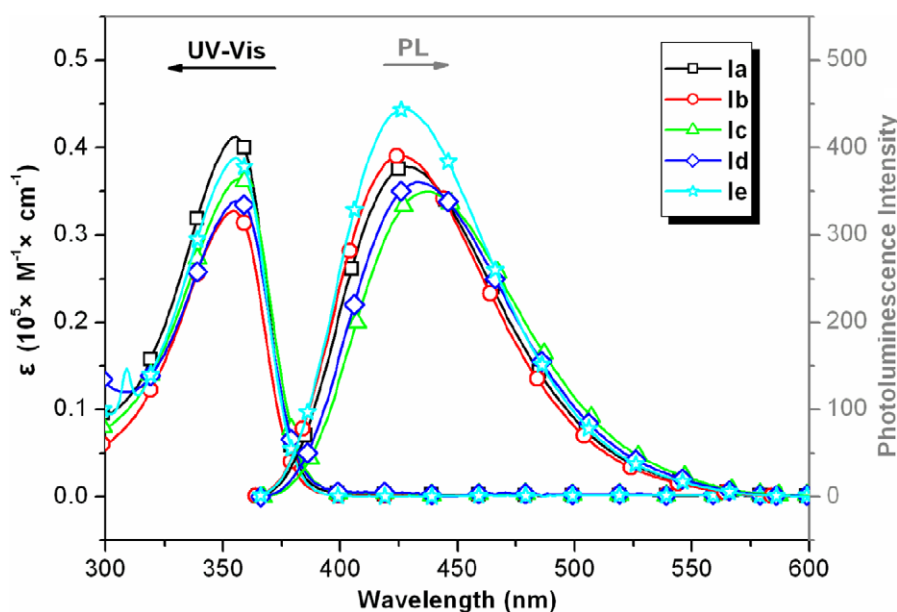

Fig. 4. UV–vis absorption and PL spectra of polyarylates in THF solution (10^{-5} M).
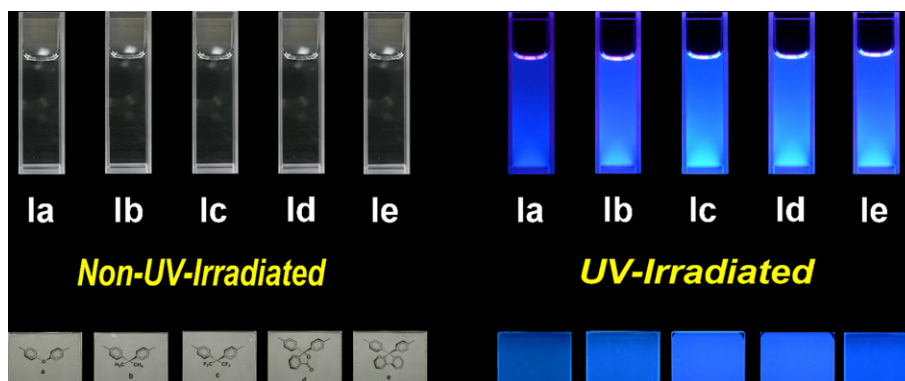

Fig. 5. The photoluminescence of polyarylates in THF solutions (10^{-5} M) and thin films (thickness: 1–3 μm) by UV irradiation (excited at 365 nm).

substituents in the bisphenol A of **Ib**, so the excited electrons will have more chance to come back to the ground state of naphthylamine chromophores. The solid-state emission spectra were similar to each other. The photoluminescence images of the polymer solution and thin film of polyarylates showed strong fluorescent blue light (Fig. 5). The UV–vis transmittance spectra of polyarylate films are also indicated in Table 4. The cutoff wavelengths (absorption edge, λ_0) from the UV–vis transmittance spectra showed light-color and high optical transparency with cutoff wavelength in the range of 385–390 nm.

In Table 4, we can see that two series of polyarylates **I** and **I′** does not exhibit significant difference in both optical and electrochemical properties except for the longer
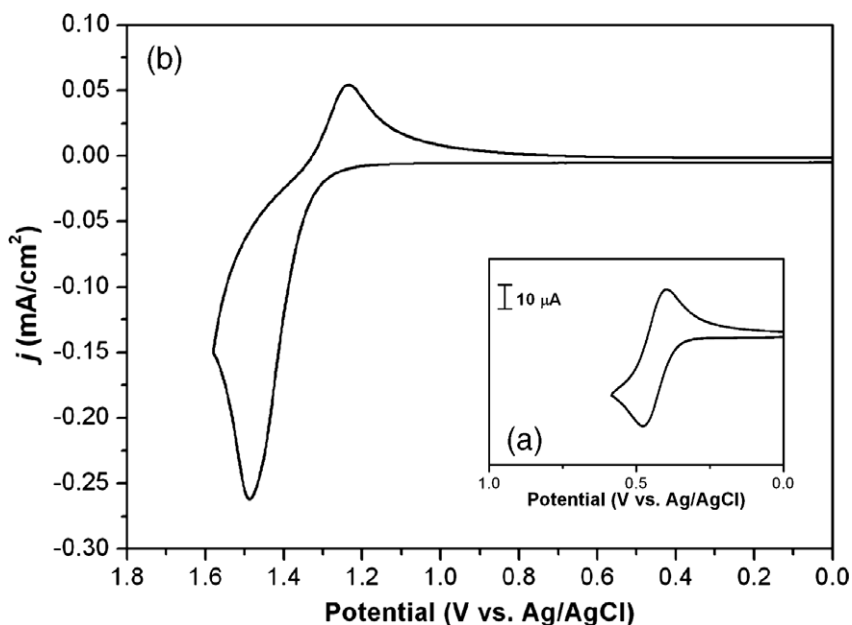

Fig. 6. Cyclic voltammograms of (a) ferrocene and (b) oxidation redox of polyarylate **Ib** film onto an indium–tin oxide (ITO)-coated glass substrate in CH$_3$CN containing 0.1 M TBAP. Scan rate = 0.1 V/s.
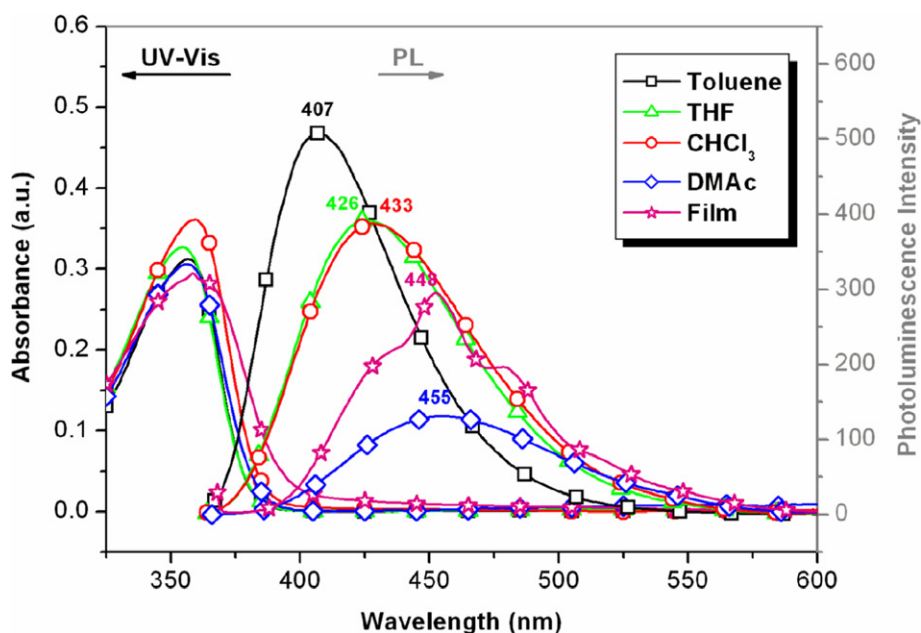

Fig. 7. UV–vis absorption and PL spectra of polyarylate **Ib** in different solvents: toluene, THF, CHCl$_3$ and DMAc (solution concentration is 10^{-5} M and excited with abs$_{max}$ respectively.)

wavelength of λ_{onset} and smaller E_g in $\mathbf{I'}$ series. That is because the pendent naphthyl group is a stronger electron withdrawing group, so that the electron which want to escape from the highest occupied molecular orbital (HOMO) state of the series $\mathbf{I}$ need more energy than $\mathbf{I'}$.

The electrochemical properties of the polyarylates were investigated by cyclic voltammetry (CV) and the data were summarized in Table 4, also. The oxidation redox behavior of these polyarylates was investigated by cyclic voltammetry conducted by the cast films on an ITO-coated glass substrate as working electrode in dry acetonitrile containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammogram for polyarylate $\mathbf{Ib}$ is shown in Fig. 6. The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the corresponding polyarylates can be determined from the oxidation onset potentials (E_{onset}) and the onset absorption wavelength of the UV–vis spectra, and the results are listed in Table 4. For example (Fig. 6), the oxidation onset potential for polyarylate $\mathbf{Ib}$ has been determined as 1.31 V vs Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard $E_{1/2}$ is 0.44 V vs Ag/AgCl in CH$_3$CN. Assuming that the HOMO energy for the Fc/Fc$^+$ standard is 4.80 eV with respect to the zero vacuum level, the HOMO and LUMO energy for polyarylate $\mathbf{Ib}$ has been evaluated to be 5.67 and 2.51 eV, respectively. The low-lying HOMO energy level of these polymers suggest that they have potential for use as hole-transporting and blue light-emitting materials in EL devices.

3.2.4. Solvatochromism

The photoluminescence spectra and images of polyarylate $\mathbf{Ib}$ were measured in different solvents (Figs. 7 and 8), and the fluorescence quantum yield (Φ_{PL}) are listed in Table 5. The absorption spectra of the four different solvents were very similar to each other. But the emission peak of the fluorescence spectra of $\mathbf{Ib}$ shifts to the longer wavelength side coincide with the increase of the polarity of the solvents was observed. The red-shift of the emission peaks, with PL emission maxima moving from 407 to 455 nm when the solvent is changed from toluene to DMAc (Fig. 7 and Table 5), which was probably due to dipole–dipole interactions of the excited state of the polymer with different solvent [24], and the fluorescence spectrum becomes broader with increasing polarity of the solvents.

The maximum fluorescence intensity of the $\mathbf{Ib}$ in toluene solution appeared at 407 nm with a highly quantum yield (Φ_{PL}) of 41.0%, which corresponds to the blue–purple light region. The maximum PL intensity of polyarylate film of $\mathbf{Ib}$ was observed at 448 nm, which is perfectly blue in color. However, the red-shifted PL spectrum of polyarylate film, compared to the fluorescence spectrum of the solution in THF, is probably due to the stronger interactions between repeating units of the polymer in the solid state [25]. This phenomenon was also previously reported in our laboratory [18].

The solvatochromism is caused by photoinduced intramolecular charge transfer (ICT) in the excited state. Such chromic behavior is associated with the stabilization of the polar emissive excited states by the polar solvents [26]. The solvatochromic shifts of the emission spectra are much larger than those of absorption spectra, implying that the excited-state energy levels are influenced more than those in the electronic ground state [27].

According to this phenomenon, we also compared the polyarylates $\mathbf{Ic}$ and $\mathbf{Ie}$ with the structural similar polyarylates $\mathbf{I'c}$ and $\mathbf{I'e}$ (bearing triphenylamine groups in the main chain based on 4,4′-dicarboxytriphenylamine) about the solvatochromic behavior, but they showed opposite photoluminescent behavior in THF and Toluene. The photophysical properties of $\mathbf{Ic}$, $\mathbf{Ie}$, $\mathbf{I'c}$, and $\mathbf{I'e}$ were measured and the results are listed in Table 6. As we know, the pendent naphthyl group is bulkier than pendent phenyl group, so we can deduce that the $\mathbf{Ic}$ and $\mathbf{Ie}$ are easier to dissolve in Toluene than $\mathbf{I'c}$ and $\mathbf{I'e}$ do. When the electrons are excited to the LUMO state, they are more likely to come back to the HOMO state of $\mathbf{Ic}$ and $\mathbf{Ie}$, just because that the HOMO state

Table 5
Photophysical properties of $\mathbf{Ib}$ in different solvents[a]

Solvent	λ_{max} (nm)	λ_{PL} (nm)	Φ_{PL} (%)[b]
Toluene	357	407	41.0
THF	354	426	34.9
CHCl$_3$	359	433	35.2
DMAc	356	455	17.1

[a] Polymer concentration of 10^{-5} M in different solvents.
[b] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H$_2$SO$_4$ with a concentration of 10^{-5} M, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24–25 °C.
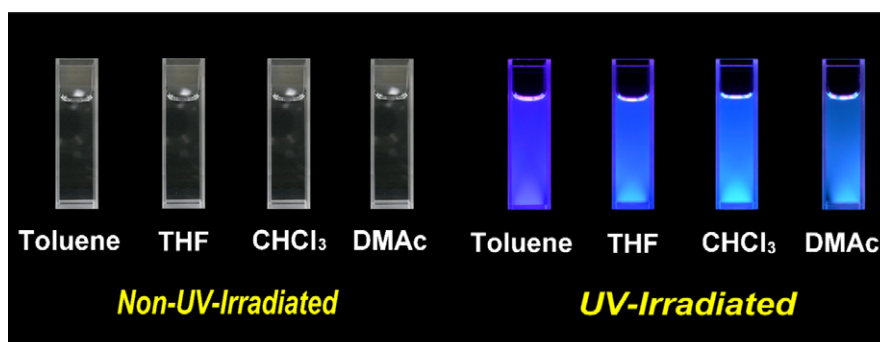

Fig. 8. The photoluminescence of polyarylate $\mathbf{Ib}$ in different solvent: toluene, THF, CHCl$_3$ and DMAc (10^{-5} M) by UV irradiation (Excited at 365 nm).

Table 6
Photophysical properties of **Ic**, **Ie**, **I′c**, and **I′e** in different solvents[a]

Code	THF			Toluene		
	$\lambda_{abs,\,max}$ (nm)	$\lambda_{PL,\,max}$ (nm)	Φ_{PL} (%)[b]	$\lambda_{abs,\,max}$ (nm)	$\lambda_{PL,\,max}$ (nm)	Φ_{PL} (%)[b]
Ic	357	437	30.4	359	414	38.6
Ie	356	428	33.4	357	409	38.7
I′c	362	433	37.7	365	413	26.6
I′e	361	425	35.2	363	407	26.3

[a] Polymer concentration of 10^{-5} M in different solvents.
[b] The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_{PL} = 0.546$).

are more stable for the electrons of **Ic** and **Ie** than they are in LUMO state. As for **I′c** and **I′e**, the excited electrons might be stabilized by the solvent and stay in the LUMO state for a longer time to result in poorer efficiency. That is maybe the reason why the two series of polyarylates exhibited opposite photoluminescent behavior in THF and toluene solution.

4. Conclusions

A novel series of blue photoluminescent aromatic polyesters (polyarylates) bearing pendent naphthylamine chromophores were synthesized from 1-[N,N-di(4-carboxyphenyl)amino]naphthalene with various bisphenols by the diphenylchlorophosphate (DPCP) activated direct polycondensation in a medium of pyridine and lithium chloride. The introduction of the bulky naphthylamine chromophores into the polymer backbone, which decreases the chain packing efficiency and increases the between-chains spaces, thus enhancing solubility, and the bulky ones do good for preserving the thermal stability of the formed polyarylates. These polyarylates were readily soluble in common organic solvents and could be cast into good quality films with moderately high T_g and thermal stability. All the polyarylates showed light color with high optical transparency from UV–vis transmittance measurement with cutoff wavelength in the range of 385–390 nm, and exhibited blue photoluminescence both in film state (446–450 nm) and in THF solution (426–437 nm). Owing to their relatively high quantum efficiency in solution, thus, these polyarylates can be considered not only as new candidates for organo-processable high-performance polymeric materials in flat panel displays (FPDs) but also could be widely applied to the blue-light-emitting materials and even the source or host for generating of hybrid white light via the intermolecular charge transfer (ICT) or intramolecular energy transfer.

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