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Synthesis and characterization of organosoluble luminescent poly(amide-imide)s

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Summary

Poly(amide-imide)s (PAIs) were synthesized from 9,9’-bis(4-aminophenyl)fluorene (APF) and different diimide-dicarboxylic acids (DIDA). The aromatic fluorene group is isolated by DIDA. The structure of the polymer was confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR. These PAIs were soluble in polar aprotic solvents, such as *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. The crystallinity of the polymers is estimated by means of wide-angle X-ray diffraction. The resultant PAIs exhibited nearly amorphous nature. Thermal stability of the PAIs was characterized by differential scanning calorimetry and thermogravimetric analysis. No obvious glass transition temperatures were detected and the 5 % weight loss temperatures of the PAIs were in the range 296–453°C in nitrogen. The optical properties were studied by Ultraviolet–visible (UV/VIS) spectra and photoluminescent (PL) in solution and film states. The results show similar absorbance and emission to those of the constituting APF monomer. The highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) were estimated from cyclic voltammograms. The values of HOMO and LUMO are -6.67 to -6.72, and -3.54 to -3.58, respectively. Their optical and electrochemical properties are not changed significantly by different DIDA.

Introduction

Polyfluorenes (PFs) have attracted considerable interest because PFs exhibits a bright blue emission and a high photoluminescence quantum efficiency.[1] However, PFs still cannot satisfy the requirements of commercial application due to inadequate lifetime and spectral stability. A defect emission is often observed, especially after prolonged operation.[2,3] In some literatures, the defect emission bands are assigned to the emission from fluorenone keto defects due to oxidation,[4,5] to the change of microscopic morphology of the films[6,7] and to the aggregate formation in the bulk materials.[8,9] Many efforts have been devoted to improve this defect, such as replacing the alkyl side chains of polyfluorene with bulky dendronic side chains[10] or benzyl-ether[11] dendrons to improve the oxidative stability.

The chromophores with lower energy gaps in fully conjugated polymers will be the emitting species via reabsorption or energy transfer because the polymers have distributed conjugation length and different energy gaps.[12] The isolated polymers, confined conjugation in a well-defined length of the chain, consists of defined hole-transporting (donor) or electron-transporting (acceptor) segments are interesting because the electron and hole affinities can be enhanced simultaneously.[13,14]

Aromatic polyimides have excellent thermal and chemical stability due to the rigid and cyclic structure of the imide group.[15] This rigid ladder-like structure of aromatic polyimides made them mostly insoluble and infusible. Much effort has been made to increase the solubility of aromatic polymers by structural modifications of aromatic polymers,[16-18] such as the introduction of bulky lateral substituents.

Aromatic poly(amide-imide)s (PAIs) have good mechanical properties at high temperature and easier processibility, and they contain desirable characteristics of both polyamides and polyimides. Bulky aromatic groups were introduced into PAIs to reduce the molecular order and enhance the solubility as well as thermal stability.[19-21]

Aromatic poly(amide-imide)s can be successfully synthesized via the direct polycondensation of imide ring containing diacids and aromatic diamines, respectively.[22,23]

In this article, aromatic poly(amide-imide)s containing isolated fluorenes were synthesized from direct polymerization of 9,9’-bis(4-aminophenyl)fluorene and different diimide-dicarboxylic acids. The synthesized polymers were characterized by infrared (IR), ^1H and ^{13}C nuclear magnetic resonance (NMR), ultraviolet/visible (UV/vis), and luminescence spectroscopies.

Experimental

Materials

Trimellitic anhydride (TMA; Wako) were used without purification. 4,4’-oxydianiline (ODA; from ACROS), 1,4-bis(4-aminophenoxy)benzene(triphenyl ether diamine-hydroquinone) (TPEQ; from TCI), 4,4’-methylenedianiline (MDA; from TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP; from Chriskev), and 9,9’-bis(4-aminophenyl)fluorene (APF; from TCI) were vacuum-distilled before use. *N*-Methyl-2-pyrrolidinone (NMP; from Merck), *N,N*-dimethylacetamide (DMAc; from Merck), dimethyl sulfoxide (DMSO; from Merck), and *N,N*-dimethylformamide (DMF; from Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Triphenyl phosphite (TPP; from TCI), xylene, and pyridine (from Merck) were used as received. Commercially available anhydrous calcium chloride ($CaCl_2$) was dried under reduced pressure at 150°C for 10 hrs. prior to use.

Instrument

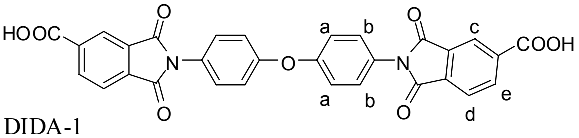
The NMR spectra of the specimen solutions in DMSO-d_6 were measured by a Bruker Avance 300 spectrometer (300 MHz). FT-IR spectra were recorded by a Perkin Elmer

Model Spectrum One spectrometer. The UV-VIS spectra of the samples in NMP were measured by a Shimadzu Model UV-160 spectrophotometer. The fluorescence spectra were recorded by a Hitach F-4500 fluorescence spectrometer. Glass transition temperature and thermal gravimetric analyses were performed on a Perkin Elmer Pyris DSC-1 and TGA-7 under a nitrogen stream and with a heating rate of 30°C/min. X-ray diffraction was measured by Shimadzu X-ray 6000 Diffractometer. The current–voltage characteristics were measured by a Keithely 2400 current/voltage source. All samples were dried in a vacuum oven at 100°C for 48 hrs. before data taking. All solid thin films of the polymers for optical characterization were prepared by spin coating onto quartz substrates from 3 wt% DMF solution and dried.

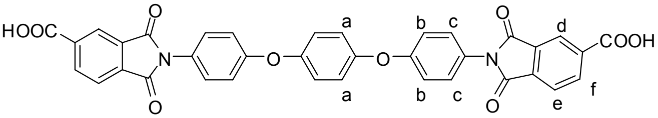
Synthesis of diimide-dicarboxylic acid (DIDA)

As a typical example, 4,4'-bis(4-trimellitimidophenyl)ether (DIDA-1) was prepared as follows: [22-24] A mixture of 20.0 g (0.1 mol) of ODA and 38.4 g (0.2 mol) of TMA was mixed in 240 g of dry NMP at room temperature for 12 h. About 50 mL of xylene was then added, and the mixture was heated at the reflux for about 5 h until about 3.6 mL of water was distilled azeotropically in a Dean–Stark trap. Heating was continued to distill the residual xylene. After cooling, the precipitated product was isolated by filtration, purified by recrystallization from NMP, and dried in a vacuum to produce 52.1 g (95% yields) of DIDA-1.

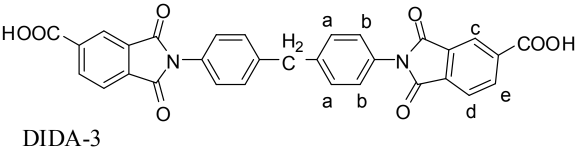
1,4-bis(4-trimellitimidophenoxy)benzene (DIDA-2), bis(4-trimellitimidophenyl) ethane (DIDA-3), and 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane (DIDA-4) were synthesized by an analogous procedure described above and the yield is higher than 95%. The chemical structures of DIADs are shown as following:



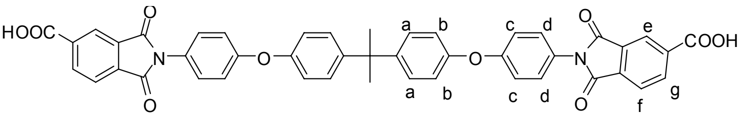
DIDA-1



DIDA-2



DIDA-3



DIDA-4

Synthesis of poly(amide- imide) (PAI)

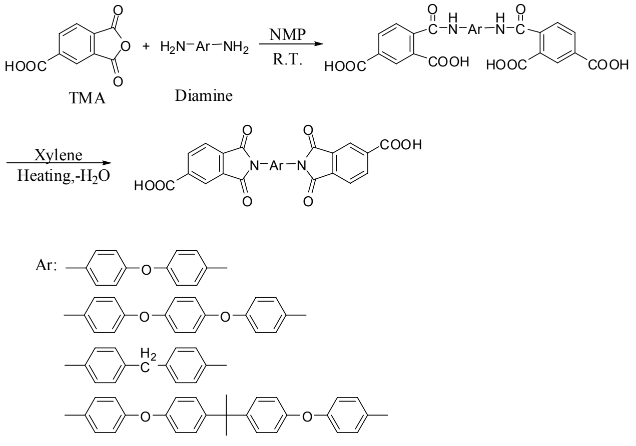
The synthesis of poly[4,4'-bis(4-trimellitimidophenyl)ether-9,9'-bis(4-amino phenyl)-fluorene] (PAI-1) is described as a typical procedure. A mixture of 3.48 g (0.01 mol) of 9,9'-bis(4-aminophenyl)fluorene (APF), 5.48 g (0.01 mol) of DIDA-1, 1 g of $CaCl_2$, 6 mL of Pyridine, 6 mL of TPP, and 30 mL of NMP was heated while being stirred at 100°C for 5 h. The viscosity of the reaction solutions increased after 30 min, and additional NMP was added to the reaction mixture. At the end of the reaction, the obtained polymer solution was trickled into stirred water. The yellow, stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under reduced pressure.

Poly(1,4-bis(4-trimellitimidophenoxy)benzene-9,9'-bis(4-aminophenyl)fluorene) (PAI-2), poly(bis(4-trimellitimidophenyl)ethane-9,9'-bis(4-aminophenyl)fluorene) (PAI-3), and poly(2,2-bis(4-(4-trimellitimidophenoxy)phenyl)propane-9,9'-bis(4-aminophenyl)-fluorene) (PAI -4) were synthesized with similar methods.

Results and discussion

Synthesis of diimide-dicarboxylic acid (DIDA)

A series of DIDAs were synthesized from TMA with ODA, TPEQ, MDA and BAPP via a two-stage procedure that included ring-opening addition of the diamine with two equivalent amounts of trimellitic anhydride in NMP, followed by cyclodehydration to the diimide–diacid by means of xylene–water azeotropic distillation (as shown in Scheme 1).



Scheme 1 Preparation of diimide-dicarboxylic acid

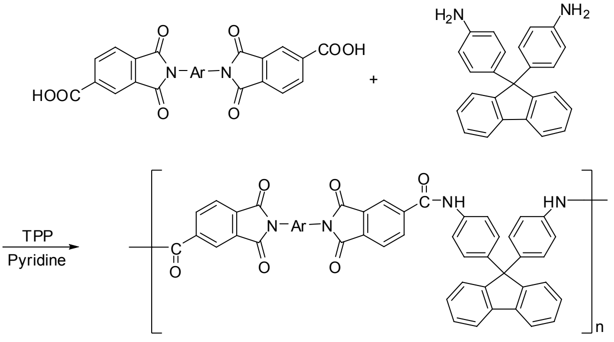
Table 1 show the characteristic absorption bands in their IR spectra and the proton resonance peaks of DIDAs. The FTIR characteristic absorptions bands of imide ring of DIDAs are observed at ca.1780, 1720, 1375, and 725 cm^{-1}. The ^1H and ^{13}C NMR spectrum are in a good agreement with the expected molecular structure.

Table 1 ^{1}H NMR, ^{13}C NMR, and IR Spectra of diimide-dicarboxylic acids (DIDAs) Synthesized from TMA with Different Diamine

DIDA	Diamine	^{1}H NMR (ppm), ^{13}C NMR (ppm), IR (cm^{-1})
DIDA-1	ODA	^{1}H NMR (DMSO-d_6, 300MHz) δ: 7.24 (4H, d, J = 8.8Hz, H_a), 7.50 (4H, d, J = 8.8Hz, H_b), 8.06 (2H, J = 7.7Hz, H_d), 8.28 (2H, s, , H_c), 8.38 (2H, d, J = 7.7Hz, H_e) ^{13}C NMR (DMSO- d_6, 75MHz) δ: 119.24, 123.54, 123.96, 127.38, 129.38, 132.21, 135.06, 135.63, 136.65, 156.17, 165.17, 166.52 IR (KBr, pellet): ν=3063, 1780, 1722, 1505, 1392, 1257, 726
DIDA-2	TPEQ	^{1}H NMR (DMSO- d_6, 300MHz) δ: 7.16 (4H, d, J = 8.9Hz, H_b), 7.18 (4H, s, H_a), 7.46 (4H, d, J = 8.9Hz, H_c), 8.06 (2H, d, J = 7.7 Hz, H_e), 8.29 (2H, s, H_d), 8.40 (2H, d, J = 7.7Hz, H_f) ^{13}C NMR (DMSO-d_6, 75MHz) δ: 118.46, 121.59, 123.36, 124.13, 127.00, 129.50, 132.45, 135.68, 136.24, 138.41, 152.48, 157.44, 166.26, 166.80 IR (KBr, pellet):ν = 3049, 1787, 1714, 1498, 1398, 1247, 727
DIDA-3	MDA	^{1}H NMR (DMSO-d_6, 300MHz)δ: 4.10 (2H, s,-CH_2-), 7.42 (8H, m, , H_a, H_b), 8.04 (2H, d, J = 7.7 Hz, H_d), 8.30 (2H, s, H_c), 8.40 (2H, d, J = 7.7Hz, H_e) ^{13}C NMR (DMSO-d_6, 75MHz) δ: 34.67, 123.78, 123.99, 127.81, 128.31, 129.62, 130.25, 132.28, 134.65, 135.78, 139.01, 166.50, 166.94 IR (KBr, pellet):ν = 3061, 2875, 1776, 1715, 1374, 1273, 1095, 726
DIDA-4	BPPP	^{1}H NMR (DMSO-d_6, 300MHz) δ: 1.66 (3H, s,-CH_3), 7.02 (4H, d, J = 8.5Hz, H_b), 7.12 (4H, d, J = 8.7Hz, H_c), 7.29 (4H, d, J = 8.5Hz, H_a), 7.44 (4H, d, J = 8.7Hz, H_d), 8.03 (2H, d, J = 7.7Hz, H_f), 8.30 (2H, s, H_e), 8.39 (2H, d, J = 7.7Hz, H_g) ^{13}C NMR(DMSO-d_6, 75MHz) δ: 31.52, 42.67, 119.27, 119.54, 124.25, 124.50, 127.51, 129.10, 129.97, 132.79, 135.29, 136.26, 146.69, 154.79, 157.52, 167.05, 167.40 IR (KBr, pellet):ν = 3408, 2967, 1783, 1727, 1601, 1502, 1379, 1242, 729

Synthesis of poly(amide- imide) (PAI)

PAIs were synthesized from 9,9’-bis(4-aminophenyl)fluorene (APF) and various DIDA by means of direct polycondensation with TPP/Pyridine as the condensing agent in NMP in the presence of calcium chloride (Scheme 2).



Scheme 2 Preparation of poly(amide-imide)s

The polymerization proceeded homogeneously throughout the reaction and precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions under stirring into water. The inherent viscosities are 0.75, 0.89, 0.82, and 0.95 dL/g for PAI-1, PAI-2, PAI-3, and PAI-4, respectively. The absorption bands of FTIR spectrum are shown in Table 2. The characteristic absorption bands for the imide ring appears at ca.1778-1779, 1717-1723 cm^{-1} (asymmetrical and symmetrical imide), 1373-1378 cm^{-1} (C-N stretching vibration), 726-737 cm^{-1} (imide ring deformation). The absorptions of amide groups appeared at 3333-3367 cm^{-1} (NH stretch) and 1663-1674 cm^{-1} (amide C=O stretch). Figure 1 shows the ^{1}H NMR spectra of PAI-1-4 in DMSO-d_6, and all the peaks have been readily assigned to the proton resonance peaks.

Table 2 The FTIR Characteristic absorbance of PAI

PAI	IR Absorbance (cm^{-1})
PAI-1	3333, 1779, 1722, 1668, 1599, 1500, 1377, 1239, 737
PAI-2	3347, 1779, 1722, 1674, 1600, 1508, 1378, 1224, 728
PAI-3	3355, 1778, 1715, 1673, 1599, 1373, 736
PAI-4	3367, 2966, 1779, 1723, 1663, 1599, 1505, 1378, 1239, 726

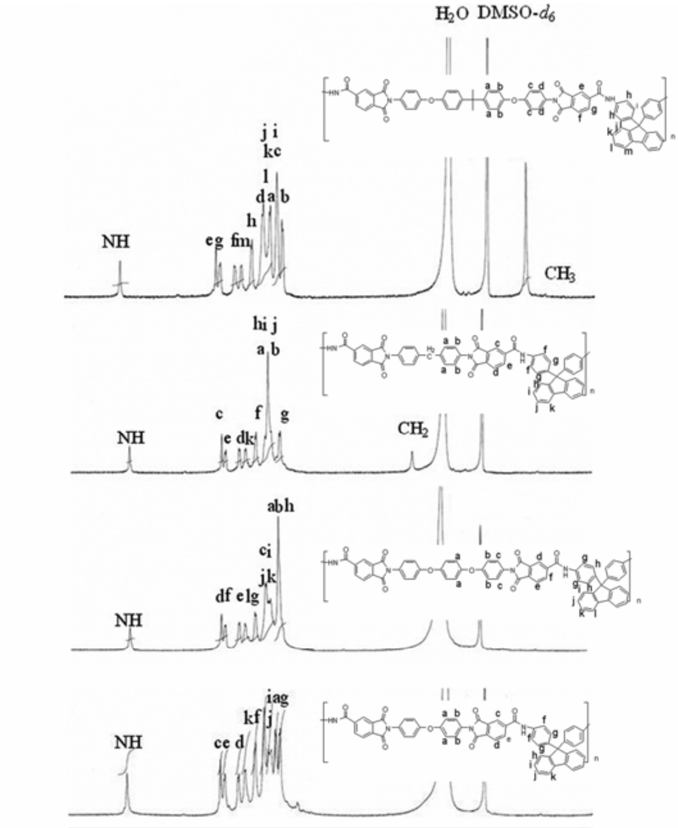


Figure 1 ^{1}H NMR spectra of PAIs.

Solubility of PAIs

Table 3 shows the solubility of PAIs in various solvents and the concentration is 0.5 g/dL. All PAIs based on APF could be easily dissolved in polar aprotic solvents such as NMP, DMAc, DMSO, and pyridine, partially dissolved in THF, and insoluble in dichloromethane (DCM) and acetone. The enhanced solubility may be attributed to the introduction of bulky fluorene group in the repeat unit. The good solubility makes these PAIs as potential candidates for practical applications by spin- or dip-coating processes.

Table 3 Solubility of PAIs

	NMP	DMSO	DMF	DMAc	THF	DCM	Acetone
PAI-1	+	+	+	+	±	-	-
PAI-2	+	+	+	+	±	-	-
PAI-3	+	+	+	+	±	-	-
PAI-4	+	+	+	+	±	-	-

[a]Measured at a polymer concentration of 0.5 g/dL in solvent

[b]Solubility: +, soluble at room temperature; ±, partially soluble or swelling; -, insoluble.

Thermal stability

The thermal stability is analyzed by DSC and TGA. A glass transition temperature (T_g) of polymers are not detected in the DSC thermograms up to the decomposition temperatures although all PAI samples are amorphous from WAXD analysis and should have a T_g.

The results of TGA analyses are shown in Figure 2 and reveal that all PAIs exhibited good thermal stability. The 5 wt% weight-loss temperatures of PAIs in nitrogen are 529, 497, 466, and 504°C, and the char yield at 800°C are 57, 70, 72, and 49 wt% for PAI-1, PAI-2, PAI-3, and PAI-4, respectively. PAI-4 exhibits a lower thermal stability because it contains aliphatic methyl groups.

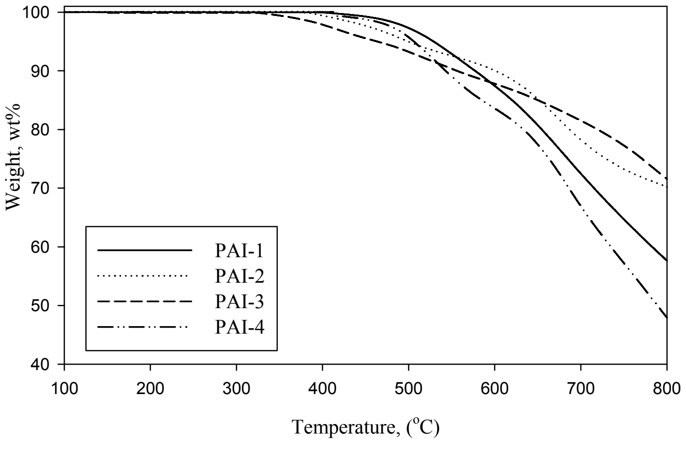


Figure 2 TGA analysis of PAIs.

Optical properties

Figure 3 shows the normalized UV/Vis and PL spectra of polymers PAIs in NMP solution (1×10^{-5} M). The maximum UV/Vis absorption (λ_{um}) and PL emission (λ_{pm}) are at 306–321 and 438–455 nm (Table 4), respectively. The absorbance and emission spectra of PAIs in solution are similar to that of constituting fluorophores, APF. The normalized UV–Vis and PL spectra of PAIs in the thin film state are shown in Figure 4. Table 4 shows the λ_{um} and λ_{pm} values in film state are around 338-350 and 445-459 nm, respectively. Both the absorption and PL spectra of all PAIs exhibited slight redshifts in the film state as compared with those in solution, probably because of the aggregation of polymeric chains.[25,26]

The energy band gap (E_g) could be estimated the following equation:

$$E_g = h\times c / \lambda_{uo} \qquad \textbf{(1)}$$

where h is the Planck constant, c is the light velocity, and λ_{uo} is the wavelength of absorption threshold. Table 4 shows the E_g values of PAIs in solution and film state. In solution, the high molecular weight of PAIs have less mobility than APF, and exhibit a little aggregation, which result in smaller E_g values. The E_g values of PAIs in film state are smaller than those of solution; it is due to the more aggregated conformation of polymer main chains solid film. In either solution or solid state, the E_g values seem not to be influenced by different DIDAs.[25-27]

Table 4 Optical Properties of the PAIs in NMP solution and film

	Solution				Film			
PAI	UV λ_{um},nm	UV λ_{uo},nm	PL λ_{pm},nm	E_g (eV)	UV λ_{um},nm	UV λ_{uo},nm	PL λ_{plm} ,nm	E_g (eV)
PAI-1	321	395	439	3.13	338	478	455	2.59
PAI-2	314	393	455	3.14	344	472	459	2.63
PAI-3	312	392	438	3.15	340	477	445	2.60
PAI-4	306	393	447	3.15	350	475	455	2.61
APF	312	356	447	3.97	--	--	--	--

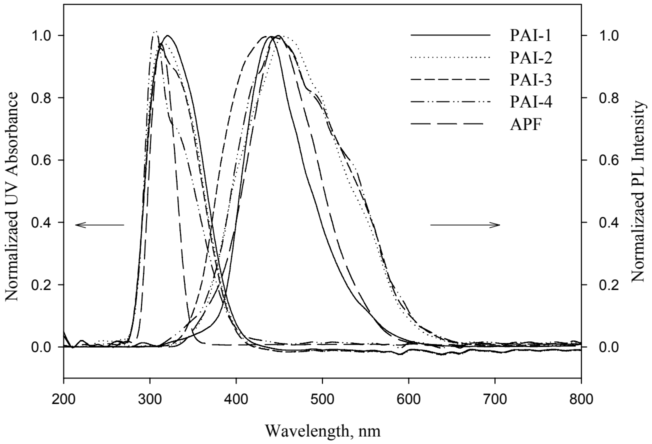


Figure 3 UV absorption and Photoluminescence spectra of PAIs (solution).

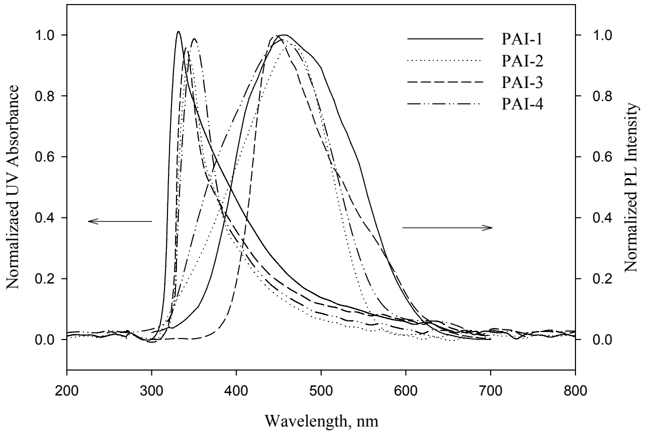


Figure 4 UV absorption and Photoluminescence spectra of PAIs (solid film).

Electrochemical properties

Figure 5 shows the cyclic voltammograms (CV) of all PAIs. The reductive behavior was conducted by the cast films on an ITO-coated glass substrate as working electrode in dry N,N-dimethylformamide (DMF) containing 0.1 M of TBAP as electrolyte. The external ferrocene/ferrocenium redox standard (FOC) is 0.45 V versus Ag/AgCl in DMF. On sweeping in cathodic direction, onset reduction potentials ($E_{re, onset}$) of PAI-1, PAI-2, PAI-3 and PAI-4 are -0.81, -0.77, -0.78 and -0.79 V, respectively. The lowest occupied molecular orbital (LUMO) energy level of PAIs can be calculated from onset reduction potentials by comparing with the ferrocence value of 4.8 eV below the vacuum level,[28] and the results are shown in Table 5. The highest occupied molecular orbital (HOMO) energy of PAIs are estimated by HOMO = LUMO $-E_g$, and the

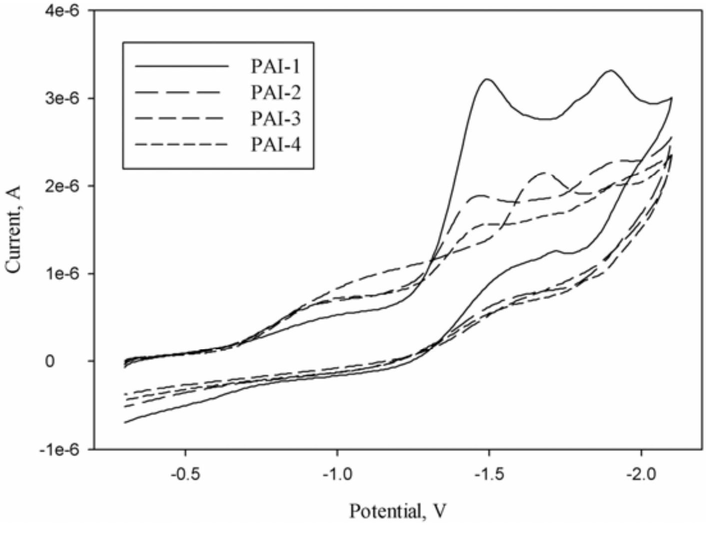


Figure 5 Cyclic voltammograms of PAIs.

results are also shown in Table 5. As can be seen in Table 5, the HOMO and LUMO are not influenced by different DIDAs.

Table 5 Electrochemical properties and band gap of PAIs

Polymer	$E_{re, onset}$ (V)	LUMO(eV)	HOMO(eV)
PAI-1	-0.81	-3.54	-6.67
PAI-2	-0.77	-3.58	-6.72
PAI-3	-0.78	-3.57	-6.72
PAI-4	-0.79	-3.56	-6.71

Conclusions

Soluble PAIs were synthesized with isolated fluorine groups in the main chain that have luminescent properties. The synthesized polymers could be dissolved in organic solvent, such as NMP, DMSO, DMF, and DMAc, and exhibited good thermal stability. The absorbance and emission peaks are close to constituted monomer, APF. The band gap (E_g), HOMO and LUMO are not changed significantly by DIDA. These PAIs solutions could be processed easily by spinning and dipping coating.

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