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Synthesis and optical properties of two series of soluble acridine-containing copolyimides

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Abstract

Two series of copolyimides were designed and synthesized by one-step polycondensation of two diamines, 3,6-diaminoacridine (Acridine) and 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA), with a dianhydride 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) or 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), respectively. The copolyimides were named as AFF*x* (Acridine-FBPA-6FDA polyimide) and AFB*x* (Acridine-FBPA-BTDA polyimide), respectively, where *x* ($x = 0$, 1, 3, 5 10, 15 and 20) represents the mole percentage of acridine among the sum of two diamines. Characterization of the polymers was conducted by using FT-IR, EA, GPC, TGA, DSC, UV–vis and FL techniques. The Mw and MWD of AFF*x* are in the range of $2.29–5.09 \times 10^4$ and 1.93–2.72, respectively, as determined using GPC. AFF*x* could be dissolved in some low boiling point solvents such as THF, CH_2Cl_2, $CHCl_3$, etc. Thin AFF*x* films could be prepared by spin coating its $CHCl_3$ or THF solution onto glass. The temperature of 10% weight loss (T_{10}) for the copolyimides was above 540 °C. The emission maximum of AFF*x* in solution at the excitation wavelength of 480 nm was near 545 nm. And that of AFB*x* solution at the excitation wavelength of 390 nm was near 525 nm. UV–vis and FL spectra of the copolyimides indicated that the main chromophores in the copolyimides were acridine moieties and the excitation energy transfer from fluorene moieties to acridine moieties could take place. The copolyimides maybe a potential thermostable light-emitting material for organic light-emitting diodes.

Keywords: Acridine; Fluorene; Copolyimide

1. Introduction

Acridine and its derivatives have been widely used as dye for applications in photovoltaic cell (PVC) [1], organic electroluminescent diode (OLED) [2], fluorescent probe [3,4], etc. Therefore, acridine-containing polymers combining the optical property of acridine and the processing ability of polymers perhaps could also be used in the application fields mentioned above.

Polyimides usually have various outstanding characteristics such as good adhesion to metal, high thermal stability, low thermal expansion, excellent film formability and especially high glass transition temperature (T_g) of above 200 °C, which make them to be potential thermostable materials for OLED. The OLED with a polyimide thin film as emissive layer [5–8] or hole transporting layer [9–11] has been successfully fabricated.

Previously, Gajiwala et al. reported the synthesis and characterization of some binary polyimides (PI) from proflavine [12] and acridine yellow [13]. Although these polyimides possessed good solubility in high boiling point solvents such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO), they still showed poor solubility in low boiling point solvents such as chloroform ($CHCl_3$) and tetrahydrofuran (THF). Furthermore, these binary polyimides have high acridine contents in the main chain, which could result in the self-quenching of acridine dye.

Recently, we have reported a novel ternary acridine-containing copolyimide AFF10, which showed high thermal stability

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and good solubility in low boiling point solvents such as $CHCl_3$ and THF. This copolyimide was prepared by the polycondensation of a dianhydride 4,4′-(hexafluoroisopropylidene)diphthalic (abbr. as 6FDA) with two diamines of 3,6-diaminoacridine (abbr. as Acridine) and 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine (abbr. as FBPA) in the molar ratio of 10/90. The electroluminescent property of AFF10 was also reported [14].

As the extension of our research for soluble copolyimide with good optical properties, we reported in the present paper the synthesis and characterization of two series of acridine-containing polyimides. Of which one series consisted of seven copolyimides from Acridine, FBPA and 6FDA, and the other was composed of seven copolyimides from Acridine, FBPA and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (abbr. as BTDA). The influence of acridine contents on the thermal stability, solubility, and optical properties of the synthesized copolyimide was discussed.

2. Experimental

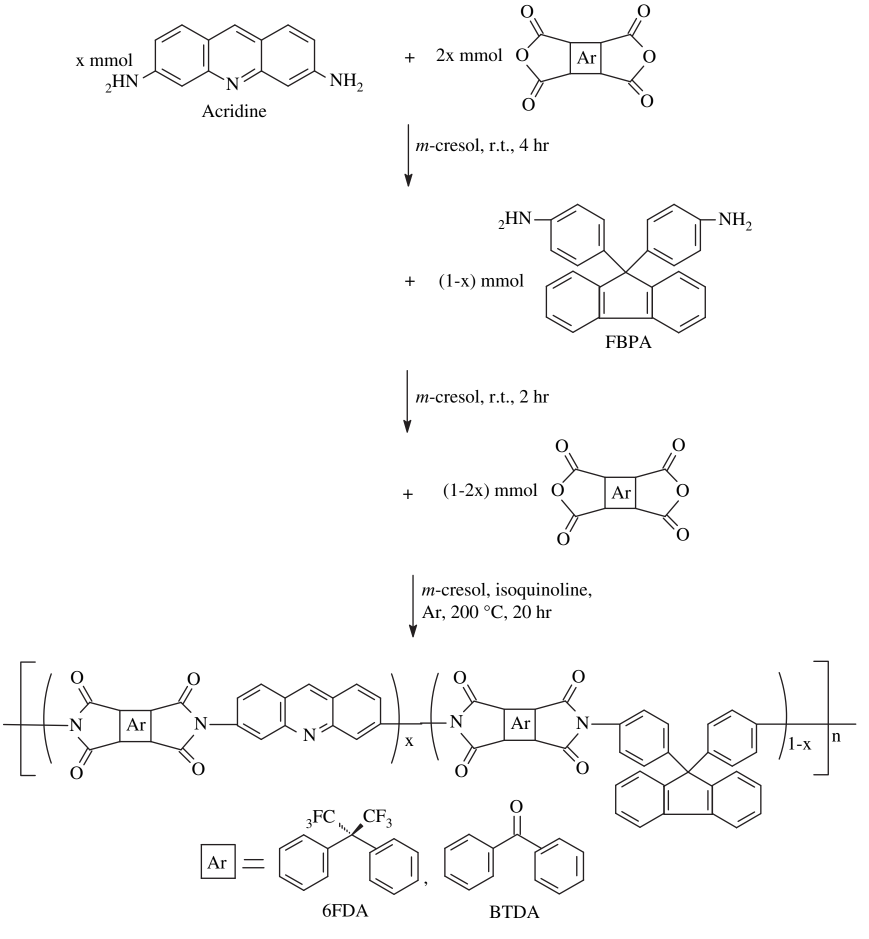
2.1. Materials

3,6-Diaminoacridine (Acridine) was purified according to the method described in the literature [12]. FBPA, 6FDA, BTDA, and phthalic anhydride (PA) were purified by sublimation. Isoquinoline was used as received. Acridine, FBPA, 6FDA and PA were purchased from Aldrich. BTDA and isoquinoline were purchased from Acros. *m*-Cresol was stored over 4 Å molecular sieves and distilled before use. Other organic solvents were commercially obtained and purified by standard distillation methods.

2.2. Synthesis of copolyimides

The copolyimides were synthesized by a one-step polycondensation of two diamines Acridine and FBPA with a dianhydride 6FDA or BTDA, respectively, as shown in Scheme 1. The molar amount of the dianhydride 6FDA (or BTDA) was kept constant, and the amounts of two diamines Acridine and FBPA were varied, while keeping the total mole number of two diamines equal to that of the dianhydride. The copolyimides originated from different comonomers were named as AFF*x* (Acridine-FBPA-6FDA polyimides) and AFB*x* (Acridine-FBPA-BTDA polyimides), where *x* ($x = 0$, 1, 3, 5 10, 15 and 20) represented the mole percentage of acridine among the sum of two diamines.

For a typical synthetic procedure, for example AFF5, the polymer was prepared in a 50 mL dried three-necked flask



AFFx: Acridine-FBPA-6FDA polyimide; AFBx: Acridine-FBPA-BTDA polyimide.

Scheme 1. Synthetic route of AFF*x* and AFB*x*.

fitted with a magnetic stirrer, a thermometer and an argon inlet/outlet adapter. Acridine of 10.5 mg (0.05 mmol) and 2 mL of *m*-cresol were charged. After complete solubilization of the diamines, 44.4 mg (0.10 mmol) 6FDA was added. The reaction mixture was stirred for 4 h at room temperature. Then, 330.8 mg (0.95 mmol) FBPA was added and the reaction mixture was stirred for another 2 h. Finally, 399.8 mg (0.90 mmol) 6FDA, 4 mL of *m*-cresol and 0.2 mL of isoquinoline were charged. The reaction mixture was stirred, heated to 200 °C and purged with a gentle argon flow for about 20 h, then gradually cooled to room temperature. The mixture was diluted with *m*-cresol during cooling to keep the mixture in a better flow state. The polymer was isolated by precipitation from 300 mL of methanol. The precipitate was filtrated and extracted with methanol in a Soxhlet extraction apparatus for 24 h. After drying under vacuum at 80 °C for 4 h and at 260 °C for 6 h, AFF5 was obtained as a gray powder with 93.5% yield.

The other copolyimides (listed in Table 1) were accessible through the same process as AFF5 by varying the molar ratios of Acridine with FBPA from 1/99 to 20/80. The yields for these polycondensation reactions were in the range of 90–95%. With the increasing acridine content in the polyimides, the color of products varied from white gray to brown.

For comparison, two binary polyimides without acridine unit, FBPA-6FDA (AFF0) and FBPA-BTDA (AFB0), were also synthesized by the method similar to that of AFF5.

2.3. Synthesis of model compound

In order to determine the absorption and fluorescence position of acridine moieties of acridine-containing polyimide, 3,6-diaminoacridine diphthalimide (abbr. as ADPI) was synthesized according to Ref. [12] and used as a model compound. The chemical structure of ADPI was confirmed by elemental analysis and FT-IR spectrum. $C_{29}H_{15}N_3O_4$ (469.1) Calcd: C, 74.2; H, 3.20; N, 8.95. Found: C, 74.1; H, 3.34; N, 8.80. FT-IR (KBr, cm^{-1}): 1786 and 1723 (the characteristic absorption bands of an imide group).

2.4. Measurements

FT-IR spectrum was recorded on a Bruker Vector 22 IR Spectrometer (KBr pellet). Elemental analysis (EA) was determined on ThermoQuest Italia S.P.A. EA 1110. Weight-average molecular weight (Mw) and molecular weight distribution (MWD) were measured on a Waters 208 Gel Permeation Chromatograph (GPC). Intrinsic viscosities were measured by using an Ubbelohde viscometer. Temperatures of decomposition (T_d) and glass transition (T_g) were determined with a Delta series TGA7 and a Perkin–Elmer Pyris 1 DSC, respectively. UV–vis absorption spectrum was recorded on a Varian Cary 100 Bio UV–vis Spectrophotometer. Fluorescence (FL) spectrum was recorded on a Hitachi F-4000 Fluorescence Spectrophotometer. Thin films of copolyimides for UV–vis and FL measurements were prepared by spin coating of polymer solution onto quartz glass using Spin Coater, Model KW-4A.

3. Results and discussion

3.1. Synthesis of copolyimide

Two series of copolyimides AFF*x* and AFB*x* were prepared by a one-step polycondensation of two diamines, Acridine and FBPA, with a dianhydride 6FDA or BTDA, respectively. As the two diamines show different reactivity, the monomers were added one by one to achieve a random incorporation of the two comonomers into the polyimide backbone. Because the synthesis process was carried out in *m*-cresol at 200 °C with a catalytic amount of isoquinoline and purged with a gentle argon flow to remove generated water, the complete

Table 1
Feed molar ratios of two diamines Acridine/FBPA, elemental analyses results, GPC[a] results and intrinsic viscosity[b] of the copolyimides

Copolyimide	Acridine/FBPA (molar ratio)	C/H/N		Mw × 10^4	MWD	[η] (dL/g)
		Calculated	Found			
AFF0	0/100	69.8/2.91/3.70	68.3/2.96/3.63	5.09	2.72	
AFF1	1/99					
AFF3	3/97			2.80	2.12	
AFF5	5/95			3.73	2.48	
AFF10	10/90	69.2/2.84/3.96	68.4/2.94/3.56	2.29	1.93	
AFF15	15/85			3.64	2.27	
AFF20	20/80	68.5/2.77/4.23	67.7/2.92/3.86	3.48	2.21	
AFB0	0/100					0.38
AFB1	1/99					0.34
AFB3	3/97					
AFB5	5/95					0.32
AFB10	10/90	78.9/3.40/4.74	77.9/3.54/4.20			0.31
AFB15	15/85					0.31
AFB20	20/80	78.3/3.33/5.08	76.8/3.54/4.61			0.28

[a] Measured at 30 °C using THF as eluent and standard polystyrene as reference.

[b] Solvent, DMF; temperature, 30 °C; concentration, 5 mg/mL.

imidization of the products could be directly achieved. The high boiling point solvent, catalyst and some oligomers could be removed by the extraction with methanol for a longer time from the crude product.

3.2. Characterization of copolyimide

Chemical structures of the copolyimides were identified by FT-IR spectra and elemental analyses. The completion of imidization was confirmed by FT-IR analyses, which were shown in Fig. 1. As shown in Fig. 1a (for AFF*x*), the characteristic absorptions of imide rings at 1784 cm^{-1} (unsymmetric stretching vibration of C=O), 1724 cm^{-1}(symmetric stretching vibration of C=O), 1369 cm^{-1} (unsymmetric stretching vibration of C–N) and 723 cm^{-1} (deformation of imide ring) were very evident [9]. The absorption at 1509 cm^{-1} was assigned to the sketch vibration of *p*-substituted phenyl ring of FBPA. And the absorption of acridine rings was overlapped by that of other phenyl rings. Moreover, as shown in Fig. 1b (for AFB*x*), the absence of O–H vibration bands at 3100–3500 cm^{-1} indicated the almost complete imidization of the polyimides.

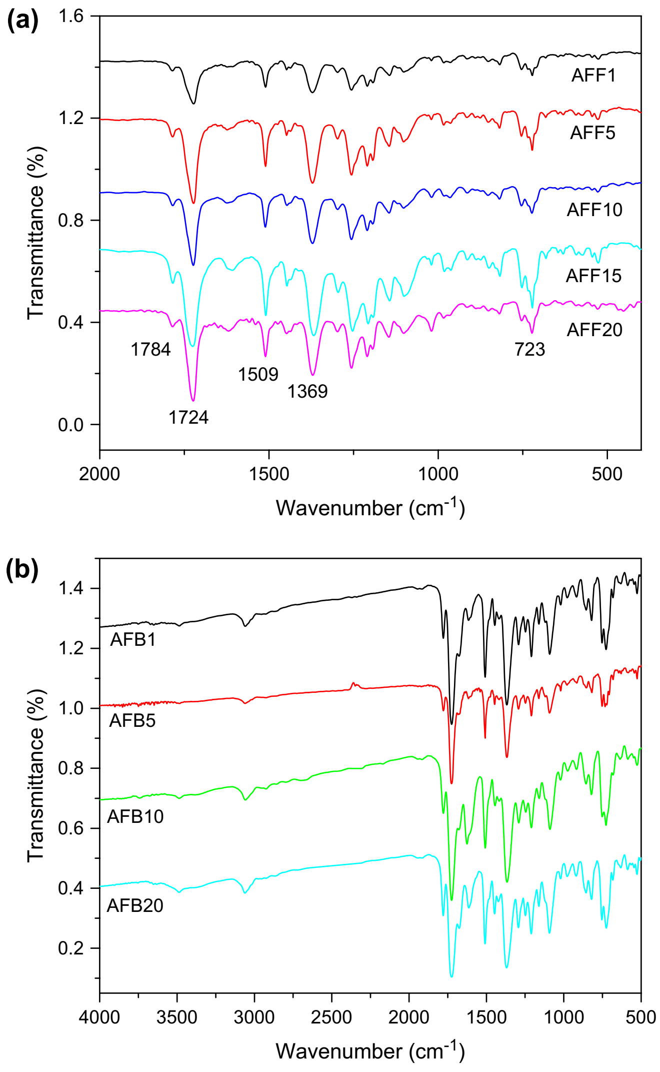


Fig. 1. FT-IR spectra of the copolyimide (KBr pellet). (a) AFF*x*; (b) AFB*x*.

Results of the elemental analyses of AFF*x* [$C_{(44-12x)}H_{(22-9x)}N_{(2+x)}O_4F_6$ $(756.5-139.0x)$], and AFB*x* [$C_{(42-12x)}H_{(22-9x)}N_{(2+x)}O_5$ $(634.5-139.0x)$] are listed in Table 1, where *x* represents the percentage of acridine among the sum of the two diamines. The measured values for C, H and N are in good agreements with the calculated values from the feed raw materials.

GPC results for AFF*x* measured at 30 °C using THF as eluent and standard polystyrene as reference are also summarized in Table 1. The Mw and MWD of AFF*x* are in the range of $2.29-5.09 \times 10^4$ and 1.93–2.72, respectively. Samples AFF0 and AFF5 show rather high deviations from MWD = 2, which probably caused by spatial inhomogeneity during the polycondensation process. On the other hand, with the increasing of Mw, the MWD increased.

As AFB*x* are only partly soluble in THF, their molecular weight could not be measured through GPC by using THF as eluent, whereupon the intrinsic viscosities of AFB*x* were measured by using an Ubbelhode viscometer with the concentration of 5 mg/mL in DMF at 30 °C. The intrinsic viscosity results are also given in Table 1, and their values are in the range of 0.28–0.38 dL/g.

The above experimental results suggested that the copolyimides were successfully prepared.

3.3. Solubility and thermal stability of copolyimide

The solubility of AFF*x* and AFB*x* was tested in some common organic solvents at room temperature, and the results are summarized in Table 2. Both AFF*x* and AFB*x* showed good solubility in some polar solvents such as NMP, DMF, DMAc and DMSO. All of them are almost not soluble in some less polar solvents such as toluene, nitromethane and acetonitrile. As a whole, the solubility of fluorine-containing AFF*x* is better than that of the corresponding AFB*x*. AFF*x* are completely soluble in THF, cyclohexanone, chloroform, DCE and TCE, while AFB*x* are partly soluble in these solvents. With the increasing acridine contents, the solubility of copolyimide decreased. Such excellent solubility of the copolymers could be attributed to the existence of both bulky diphenylfluorene moieties and flexible moieties in the polymer main chain. The bulky diphenylfluorene moieties make a severe steric hindrance to decrease the molecular interactions and also provide an easier pathway for solvent. The flexible moieties, hexafluoroisopropylidene groups ($-C(CF_3)_2-$) for AFF*x* and carbonyl groups (C=O) for AFB*x*, could increase the chain flexibility and the affinity of polymer chain to polar solvents [15,16]. As the flexibility and affinity of hexafluoroisopropylidene groups are larger than that of carbonyl groups, the solubility of AFF*x* is better than that of AFB*x*.

The thermal properties of copolyimides were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal stability of copolyimides was evaluated by TGA measurements in nitrogen atmosphere at a heating rate of 10 °C/min. The TGA curves of AFF*x* and

Table 2
Solubility of the copolyimides (10 mg/mL) at room temperature

Solvents[a]	Solubility[b]													
	AFF0	AFF1	AFF3	AFF5	AFF10	AFF15	AFF20	AFB0	AFB1	AFB3	AFB5	AFB10	AFB15	AFB20
THF	+	+	+	+	+	+	+	±	±	±	±	±	±	±
Cyclohexanone	+	+	+	+	+	+	+	±	±	±	±	±	±	±
Chloroform	+	+	+	+	+	+	+	+	+	+	±	±	±	±
DCE	+	+	+	+	+	+	+	+	+	+	+	±	±	±
TCE	+	+	+	+	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DMAc	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Toluene	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Nitromethane	−	−	−	−	−	−	−	−	−	−	−	−	−	−
Acetonitrile	−	−	−	−	−	−	−	−	−	−	−	−	−	−

[a] THF, tetrahydrofuran; DCE, dichloroethane; TCE, 1,1,2,2-tetrachloroethane; NMP, *N*-methyl-2-pyrrolidone; DMF, *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethylacetamide; DMSO, dimethyl sulfoxide.

[b] Solubility: +, soluble; −, insoluble and ±, partly soluble.

AFB*x* are shown in Fig. 2. The temperature of 10% weight loss (T_{10}) for both AFF*x* and AFB*x* was above 540 °C. Furthermore, DSC curves of the copolyimides were measured in nitrogen atmosphere at a heating rate of 20 °C/min. No apparent glass transition was observed from their DSC curves (the inset in Fig. 2) below 350 °C. Such high thermal stability of copolyimides can also be attributed to the existence of bulky diphenylfluorene moieties in the polymer backbone [15,16].

3.4. UV–vis absorption spectra of copolyimides

UV–vis absorption and fluorescence spectra of the copolyimides were measured both in solution and in film states. All the solution concentrations of copolyimides for UV–vis absorption and fluorescence spectra measurements were 0.04 mg/mL. Thin films of AFF*x* were prepared by spin coating of AFF*x* chloroform solution (20 mg/mL) on a quartz glass at 2500 rpm for 30 s at room temperature.

UV–vis spectra of Acridine (3,6-diaminoacridine), ADPI, AFF20 and AFB20 in solution are shown in Fig. 3. For Acridine (monomer), the absorption maximum is at 462 nm. As for ADPI, the absorption maximum of acridine moieties shifted to 370 nm (about 92 nm hypsochromic shift), which perhaps resulted from the replacement of two amino groups neighbouring acridine ring with two imide groups. As imide group is electron-accepting group and amino group is electron-donating group, the replacement of amino group with imide group can decrease the conjugated length of acridine moieties. Comparing the absorption spectra of AFF20 and AFB20 with that of ADPI, the absorption maximum at 370 nm for AFF20 and at 390 nm for AFB20 could be ascribed to the absorption of acridine moieties. The peak at 308 nm of the two polyimides originated from the absorption of fluorene moieties.

UV–vis absorption spectra of AFF*x* and AFB*x* in chloroform solution are shown in Fig. 4a and b, respectively. For AFF*x* (Fig. 4a), three absorption peaks at 247 (with a shoulder

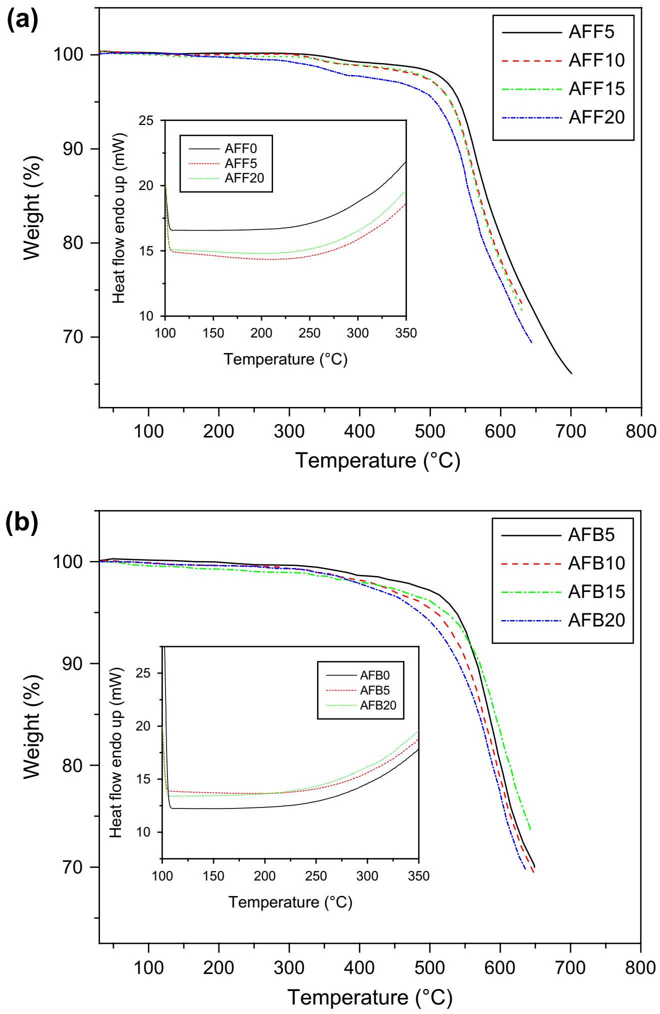


Fig. 2. TGA and DSC (inset) curves of the copolyimides in nitrogen atmosphere at a heating rate of 10 °C/min for TGA and 20 °C/min for DSC. (a) AFF*x*; (b) AFB*x*.

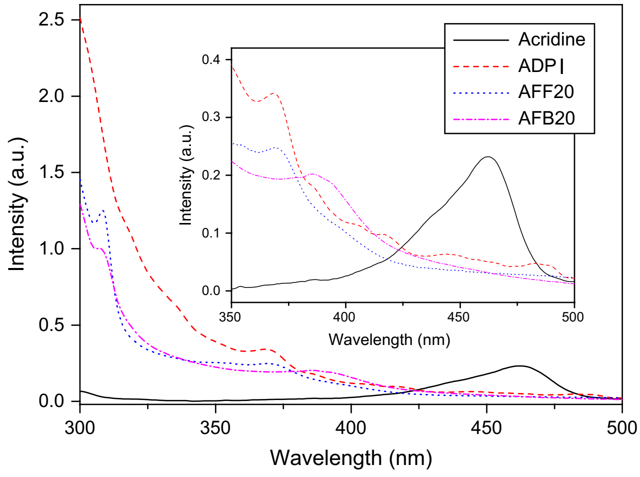


Fig. 3. UV–vis absorption spectra of Acridine, ADPI, AFF20 and AFB20 in solution in 300–500 nm (inset figure is in 350–500 nm).

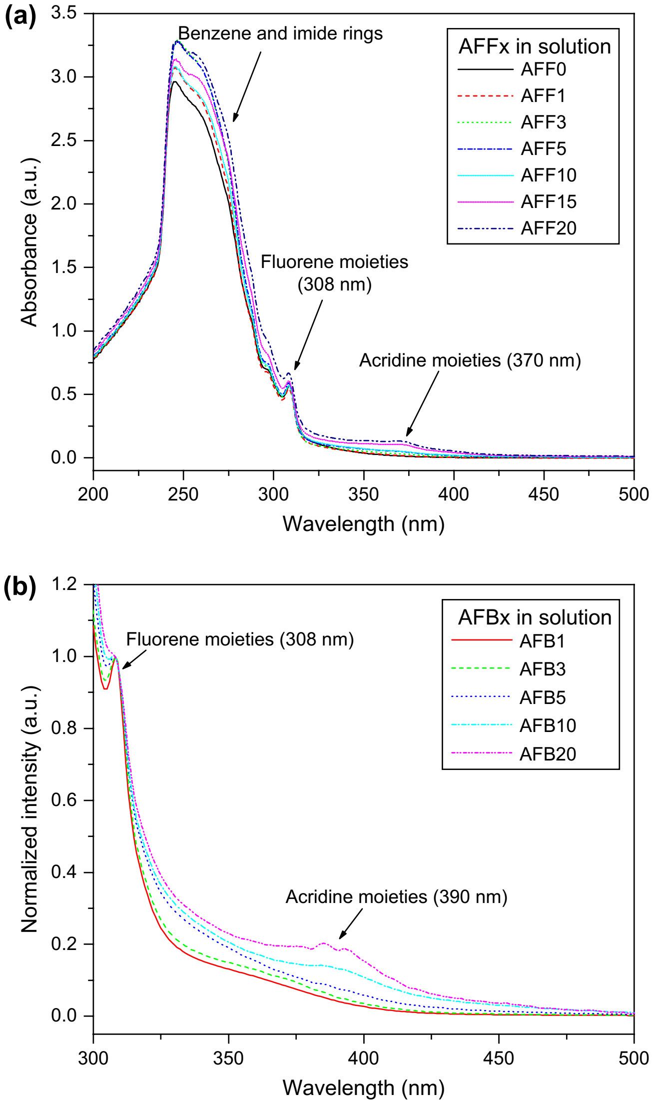


Fig. 4. UV–vis absorption spectra of the copolyimides in solution. (a) AFF*x*; (b) AFB*x*.

peak at 260 nm), 308 and 370 nm were observed. Comparing Fig. 4 with Fig. 3, the peak at 370 nm could be assigned to the absorption of acridine moieties. The peak at 308 nm could be attributed to the absorption of fluorene moieties. And the absorption bands at 247 nm may originate from the absorption of benzene and imide rings. As for AFB*x* (Fig. 4b), although the absorption of fluorene moieties was also at 308 nm, the absorption maximum of acridine moieties shifted to 390 nm.

Fig. 5 shows the UV–vis absorption spectra of AFF*x* in films on quartz glass. The spectra consisted of four peaks with central wavelength at 213, 264, 309, 374 nm. The two peaks at 309 and 373 nm resemble the UV–vis absorption spectra of AFF*x* in solution, which also could be attributed to the absorption of fluorene moieties and acridine moieties, respectively. But the spectra in the range of 200–300 nm quite differ from those in solution, which may originate from the presence of intra- and interchain charge transfer complexes (CTC) in film state [17].

3.5. Fluorescence spectra of copolyimides

Although the Acridine monomer solution emits very strong fluorescence under irradiation of ultraviolet light, the fluorescence of ADPI and copolyimides solution was very weak. The fluorescence (FL) spectra of Acridine and ADPI in solution are shown in Fig. 6. For Acridine, the emission spectrum at the excitation wavelength of 463 nm has only one peak at 490 nm, which is symmetrical to the excitation spectrum at the emission wavelength of 490 nm. While for ADPI, the emission spectrum at the excitation wavelength of 380 or 480 nm has one peak at 532 nm with a shoulder peak at 568 nm, but the excitation spectrum at the emission wavelength of 530 nm is very complicated. The fact that the emission spectrum of ADPI has only one peak indicated that there was only one kind of chromophore (acridine moieties) in ADPI. Comparing the FL spectrum of ADPI with that of Acridine, about 42 nm red shift occurs.

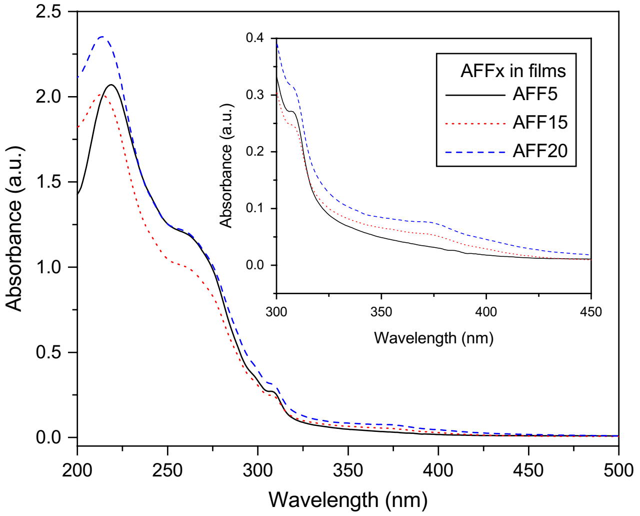


Fig. 5. UV–vis absorption spectra of AFF*x* in films on quartz glass in 200–500 nm (inset figure is in 300–450 nm).

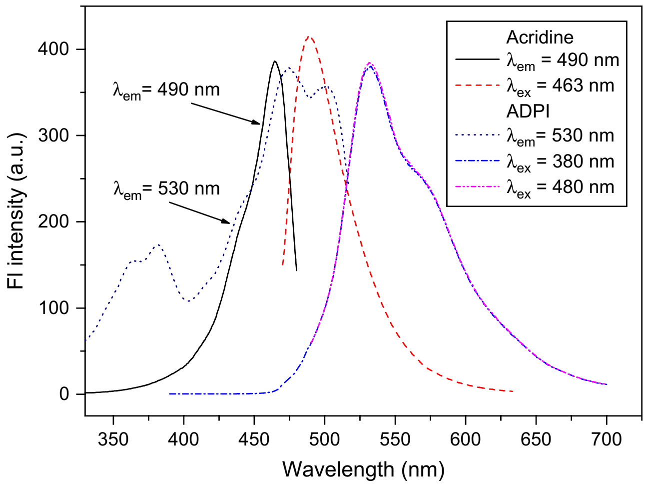


Fig. 6. FL spectra of Acridine and ADPI in solution.

Fig. 7 shows the FL spectra of AFF15 and AFF*x* in solution. As shown in Fig. 7a, the excitation spectrum of AFF15 at the emission wavelength of 540 nm consisted of three peaks at 295, 382 and 490 nm. The emission spectrum at the excitation wavelength of 295 or 308 nm consisted of a peak at 545 nm and a shoulder peak at 467 nm. The emission spectrum at the excitation wavelength of 380 nm consisted of two peaks at 545 and 450 nm. When AFF15 solution was irradiated by 480 nm light, the emission spectrum consisted of one peak at 544 nm. Comparing the emission spectra at different excitation wavelengths with each other, the peak at 545 nm occurred all the time. Then comparing the emission spectra of AFF15 solution with that of ADPI solution, the peak at 545 nm may originate from the emission of acridine moieties, while the other peaks may originate from the emission of some intra- and interchain CTC. Therefore, when 480 nm light was chosen to excite AFF*x* solution, the emission spectra should only originate from the emission of acridine moieties. As shown in Fig. 7b, the emission spectra of all AFF*x* series in solution had one peak with emission maximum near 545 nm. With the increasing acridine contents in the copolyimides, a slight red shift was observed.

Fig. 8 shows the FL spectra of AFB15 and AFB*x* in solution. As shown in Fig. 8a, the excitation spectrum at the emission

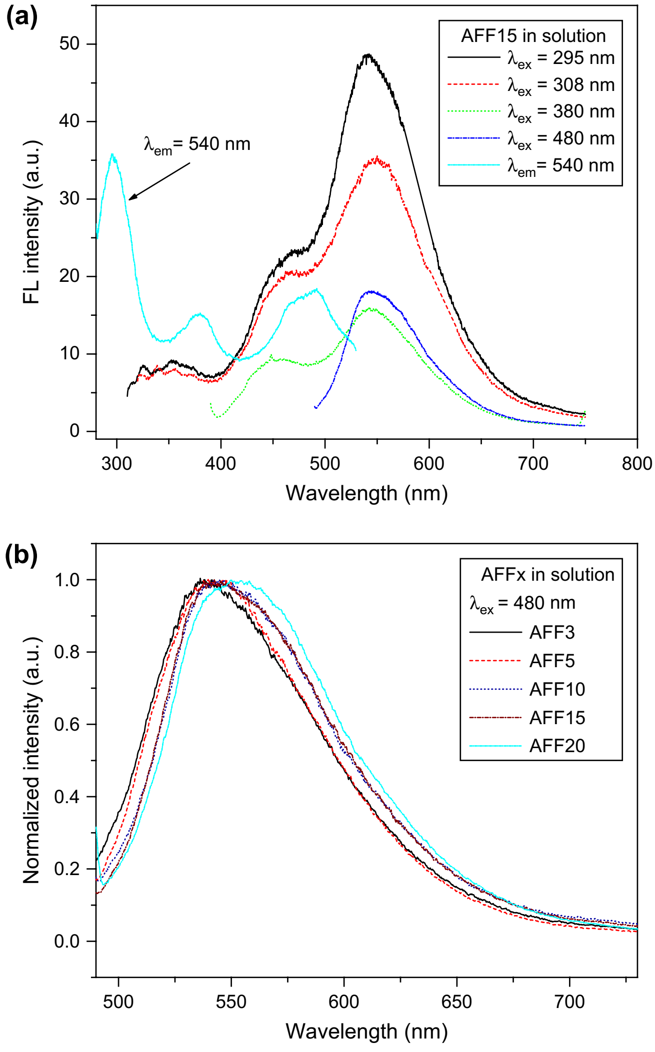


Fig. 7. FL spectra of AFF*x* in solution. (a) AFF15; (b) AFF*x*.

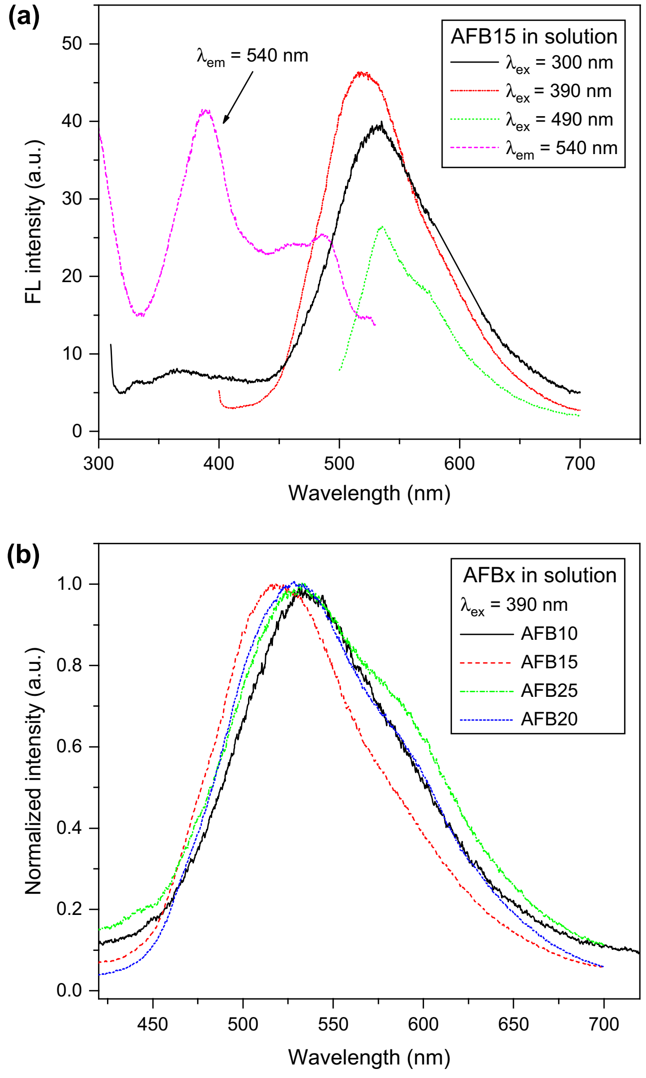


Fig. 8. FL spectra of AFB*x* in solution. (a) AFB15; (b) AFB*x*.

wavelength of 540 nm has two peaks in the range of 300–530 nm, and the fluorescence intensity of the peak at 388 nm is stronger than that of the peak at 487 nm. While in the emission spectrum of AFF15, the peak at 382 nm is weaker than that of the peak at 490 nm. When AFB15 solution was excited by 390 nm light, its emission spectrum consisted of one peak at 518 nm, which is different from that of AFF15 at the excitation wavelength of 380 nm. When AFB15 solution was excited by 480 nm light, the fluorescence intensity was much weaker than that at the excitation wavelength of 390 nm. Therefore, 390 nm light was chosen to excite AFB*x* solution. As shown in Fig. 8b, the emission spectra of AFB*x* solution at the excitation wavelength of 390 nm have one peak at 525 nm.

Fig. 9 shows FL spectra of AFF15 and AFF*x* in films on quartz glass. As shown in Fig. 9a, the excitation spectrum at the emission wavelength of 535 nm of AFF15 film has two weak peaks at 377 and 487 nm. When AFF15 film was excited by 380 nm light, the emission spectra consisted of two peaks at 438 and 545 nm, and the fluorescence intensity of the peak at 438 nm was much stronger than that at 545 nm, which was quite dissimilar to that of AFF15 in solution at the same excitation wavelength (Fig. 7a). When AFF15 film was excited by 480 nm light, the fluorescence is weak and the emission spectrum has only one peak at 532 nm. Furthermore, when AFF15 film was excited by 308 nm light, the fluorescence is strong and the emission spectra have one peak with the central wavelength at 558 nm and a shoulder peak at 443 nm, which are similar to that of AFF15 in solution. Since no new peak in the range of 300–500 nm in film state (see Fig. 5) occurred, the difference of AFF15 FL spectra in different states may result from the chain packing in film state, which resulted in the extent of interchain CTC in film state was much higher than that in solution. As shown in Fig. 9b, the emission spectra at the excitation of 480 nm of all AFF*x* series in films state have one broad peak with emission maximum nearer to 540 nm. With the increasing acridine contents in the copolyimides, no apparent change was observed in their fluorescence spectra.

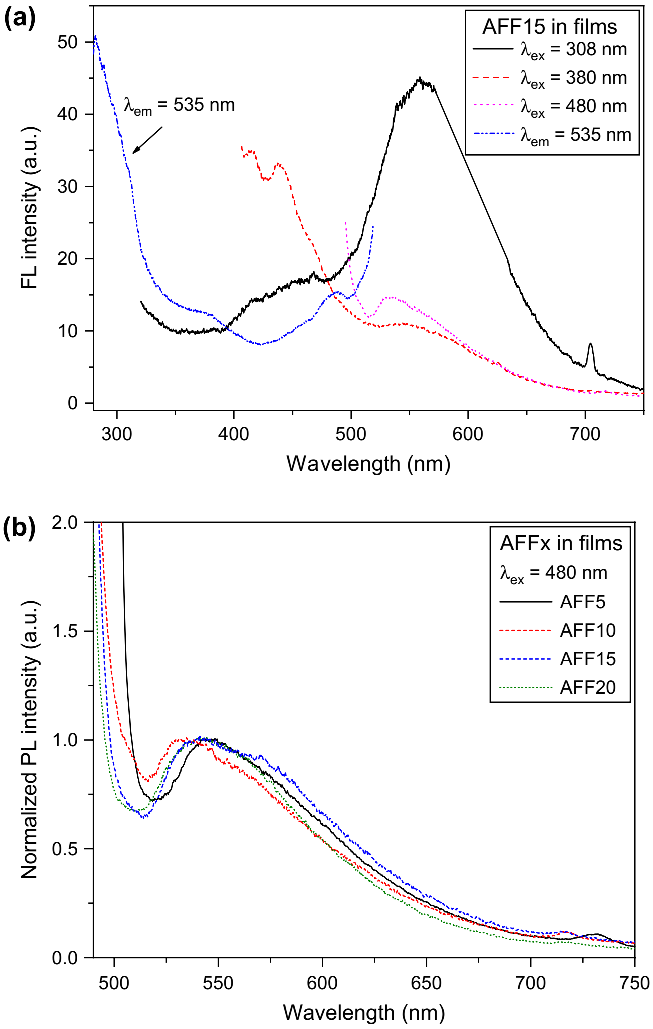


Fig. 9. FL spectra of AFF*x* in films on quartz glass. (a) AFF15; (b) AFF*x*.

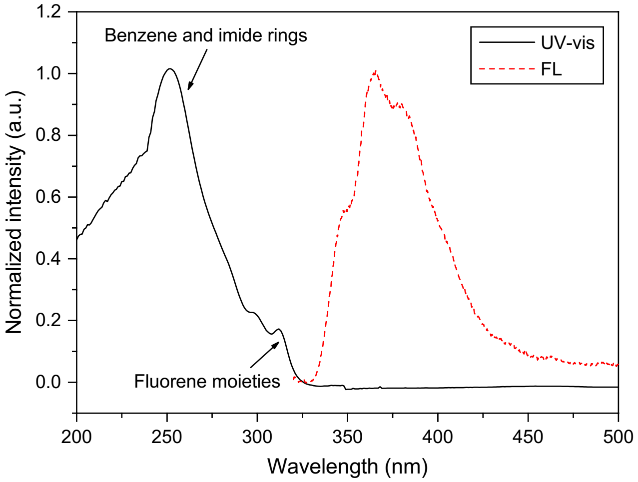


Fig. 10. UV–vis and FL ($\lambda_{ex} = 308$ nm) spectra of AFF0 in solution.

Fig. 10 shows UV–vis and FL spectra of AFF0 in solution. As shown in UV–vis absorption spectrum, the peak at 308 nm originated from the absorption of fluorene moieties. When AFF0 solution was irradiated by 308 nm light, the emission peak at 348, 365 and 377 nm originated from the emission of fluorene moieties. However, when AFF*x* were irradiated by 308 nm light in solution (Fig. 7a) or in solid state (Fig. 9a), the emission of fluorene moieties was very weak and the emission spectra mostly constituted of the emission of acridine moieties. As the acridine moieties do not directly absorb 308 nm light (Figs. 4 and 5), excitation energy transfer from fluorene moieties to acridine moieties must take place.

4. Conclusions

Two series of acridine-containing copolyimides AFF*x* and AFB*x* were designed and successfully synthesized. The copolyimides have high thermal stability and good solubility in common solvents such as chloroform and THF, which mainly resulted from the bulky side group, diphenylfluorene group, in the polyimide backbone. Thin AFF*x* films could be easily prepared by spin coating its chloroform or THF solution onto glass. UV–vis and FL spectra of the copolyimides indicated that the main chromophores in the copolyimides were acridine moieties and the excitation energy transfer from fluorene moieties to acridine moieties could take place. Therefore, the copolyimides maybe a potential thermostable light-emitting material for OLED.

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