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Synthesis and characterization of novel poly(aryl ether ketone)s with metallophthalocyanine pendant unit from a new bisphenol containing dicyanophenyl side group

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Abstract

A new bisphenol, (3,4-dicyano)phenylhydroquinone was prepared via a three-step reaction. Then a series of novel poly(aryl ether ketone) copolymers containing dicyanophenyl groups were prepared by the reactions of 4,4′-difluorobenzophenone with (3,4-dicyano)phenylhydroquinone and 4,4′-isopropylidenediphenol. After that, a series of poly(aryl ether ketone)s with metallophthalocyanine pendants were synthesized via the reactions of poly(aryl ether ketone)s containing dicyanophenyl with excessive amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. These resulting copolymers were found to have high glass transition temperatures and high thermal stability. They have good solubility and are capable of forming tough films. These copolymers show strong optical absorption in the visible region and exhibit strong blue photoluminescence.

Keywords: Synthesis; Poly(aryl ether ketone) copolymer; Metallophthalocyanine

1. Introduction

Since the synthesis of phthalocyanines in the early 1930s [1], technologies associated with these compounds have been developed around these interesting materials. There are literally thousands of publications and patents related to phthalocyanine and its analogs [2–4]. Owning to their application in optical data processing and catalytic activity, recently, there has been renewed interest in phthalocyanine compounds [5–15]. Nevertheless, it is difficult for most phthalocyanine compounds to dissolve and to melt, which results in the restriction in their applications. It is an effective method to enlarge the scope of their application through introducing a phthalocyanine compound to a polymer to result in a phthalocyanine polymer that possesses better solubility and processibility.

Various phthalocyanine polymers, for example, stacked polyphthalocyanines for electroconductors [16,17], thermally stable polymers containing metallophthalocyanine groups [18], copolymerized phthalocyanine polymers for organic photoconductors [19,20], phthalocyanine polymers for catalyzers [21,22], and so on, have already been prepared. Moreover, it was also reported that metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from phthalonitrile end-capped polymers [23–27]. These polymers have high T_gs and are soluble in common organic solvent. Some metals, such as Cu, Zn, Fe, Ni and Co were used in the above preparation. These phthalocyanine polymers can be potential candidates as electroluminescent and electron transport materials.

In the present paper, we focus our attention on the synthesis of a new bisphenol containing dicyanophenyl groups via a three-step synthetic procedure. Base on this monomer, a series of PAEKs copolymers containing dicyanophenyl groups were synthesized. Because the new bisphenol contains dicyanophenyl pendant groups, the polymers derived from it may possess good solubility and consequently may be processed in solution. We report herein the synthesis of the novel PAEKs containing dicyanophenyl and metallophthalocyanine pendant groups by using the new bisphenol as the starting material, and the characterization of these polymers by means of GPC, IR, TGA, DSC, UV–visible and fluorescence spectroscopy.

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2. Experimental

2.1. Materials

Phthalonitrile (Adrich Chemicals Inc), 4,4′-isopropylidenediphenol (BPA) (Shanghai Chemical Reagent), 1,4-benzoquinone (Dalian Jinzhou Chemical). Zinc powder, quinoline, toluene, chloroform, methanol, acetone, *N*,*N*-dimethylacetamide (DMAc), ethanol, *n*-butanol, sodium nitrite, sodium bicarbonate and concentrated hydrochloric acid (36%) were obtained from commercial sources and used as received. 4,4′-Difluorobenzophenone and 4-amidophthalonitrile were prepared in our lab according to the standard procedure.

2.2. Instrumentation

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 510 instrument with dimethylsulfoxide-d_6 (DMSO-d_6) as the solvent. The FTIR spectra were recorded via the KBr pellet method by using a Nicolet Impact 410 FTIR spectrophotometer. The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The inherent viscosity measurements were carried out with an Ubbelohde viscometer in concentrated sulfuric acid at 25± 0.1 °C. The gel permeation chromatography (GPC) analysis was carried with a Waters 410 instrument with tetrahydrofuran as the eluent and polystyrene as the standard. The glass transition temperatures (T_gs) were determined by using a modulated DSC (Model Mettler DSC821^e) instrument at a heating rate of 20 °C/min under a nitrogen flow of 100 mL/min. The reported T_g values were recorded during the second scan. The thermo gravimetric analysis was performed on a Perkin–Elmer Pryis 1 TGA analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 20 °C/min. The UV–visible absorption spectrum was recorded on a UV2501-PC spectrophotometer and the fluorescence measurements were carried out with an LS 55 spectrophotometer.

2.3. Synthesis

2.3.1. Synthesis of (3,4-dicyano)phenyl hydroquinone (**3**)

Into a 1000 mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer were placed water (50 mL), ice (50 mL) and compound **1** (5.575 g, 0.025 mol). Hydrochloric acid (11.8 M, 21 mL) was added dropwise into the stirred mixture through the dropping funnel, and then a concentrated water solution of sodium nitrile (1.725 g, 0.025 mol) was added dropwise. The mixture was stirred for 2 h at 0–5 °C, and a clear solution was yielded. The resulting solution was filtered and added dropwise to the mixture of 1,4-benzoquinone (2.16 g, 0.02 mol), sodium bicarbonate (16.8 g, 0.2 mol), and water (100 mL). The reaction mixture was stirred at 10–15 °C for about 2 h and then at room temperature for 2 h. Next, the precipitate was collected by filtration, washed thoroughly with water and at 60 °C in a vacuum oven. The product as brown crystals was obtained via recrystallization from *n*-butanol.

Compound **2** (2.34 g, 0.01 mol), Zn powder (1.95 g, 0.03 mL), and 40 mL of the mixture water and ethanol (1:1, v/v) were placed into a 100 mL, three-necked flask equipped with a mechanical stirred, a condenser and a dropping funnel. The mixture was heated to 90 °C with stirred, which was followed by the dropwise addition of 6.8 mL of hydrochloric acid (11.8 M) dropwise at a rate of 0.5 drops per second. After the addition being completed, the reaction mixture was allowed to reflux for 3 h. Then, the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected and recrystallized from the mixture of water and ethanol (6:4, v/v).

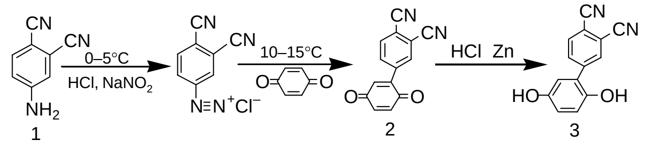
Yield: 80%. Mp: 260–263 °C (DSC). *m*/*z*: 236. Elem. Anal. Calcd for $C_{14}H_8N_2O_2$ (236.23 g/mol): C, 70.74%, H, 3.57%, N 11.57%. Found: C, 71.18%, H, 3.41%, N, 11.86%. IR (KBr, cm^{-1}): 3308 (–OH), 2245 (–CN). ^{1}H NMR (DMSO-d_6, δ, ppm): 9.37 (s, 1H), 9.00 (s, 1H), 8.27 (s, 1H), 8.14 (d, $J=$ 8.5 Hz, 1H), 8.08 (dd, $J=8.5$ Hz, 1H), 6.83 (d, $J=8.5$ Hz, 1H), 6.77 (s, 1H), 6.73 (d, $J=8.5$ Hz, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm). 150.36, 147.07, 144.16, 133.98, 133.68, 123.99, 117.55, 117.21, 116.19, 116.05, 114.35, 111.87.

2.3.2. General procedure for synthesis of polymers (**4**)

The procedure for synthesis of a series of copolymers **4** is as follows. To a 100 mL three-neck round-bottom flask equipped with a mechanical stirrer, a Dean–Stark trap, a condenser, and a nitrogen inlet, were added monomer **3**, BPA, DMAc, K_2CO_3, and toluene. Under an atmosphere of nitrogen, the solution was heated to 130–140 °C and maintained at that temperature for 2 h to remove all water by means of a Dean–Stark trap through toluene. The polycondensation reaction was continued for 6 h at 150–160 °C. Then the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized into a powder after cooling. Next, the powder was washed with hot methanol and water several times and dried at 110 °C under vacuum for 24 h. The copolymers were prepared with varying the mole fraction of **3** (n) and that of BPA (m). The copolymers with different n/m ratios, viz., 5:95, 10:90, 20:80, and 40:60 were prepared and designated as **4a**, **4b**, **4c** and **4d**, respectively.

2.3.3. Procedure for synthesis of copolymers containing metallophthalocyanine (**5**)

For the synthesis of the copolymers containing metallophthalocyanine, copolymer **4c** was selected. The general procedure is as follows. To a 250 mL three-neck flask equipped with a condenser and a nitrogen gas inlet, were added copolymer **4c**, phthalonitrile, the corresponding metal chloride (in the present work, copper, zinc, cobalt, iron and nickel chloride were used), and 150 mL of quinoline. Under an atmosphere of nitrogen, the mixture was heated to 210–220 °C for 6 h. After this period, the reaction mixture became dark blue. Then the mixture was poured into a mixture of 300 mL of methanol and 20 mL of hydrochloric acid (11.8 mol/L) under vigorous stirring. The precipitated particles were washed with acetone, ethanol and water. Then the precipitate was collected by filtration and extracted by chloroform with a Soxhelt



Scheme 1. Synthesis of (3,4-dicyano)phenyl hydroquinone.

extractor. The chloroform solution was concentrated and precipitated in methanol. A polymer was produced and dried at 110 °C for 24 h.

3. Results and discussion

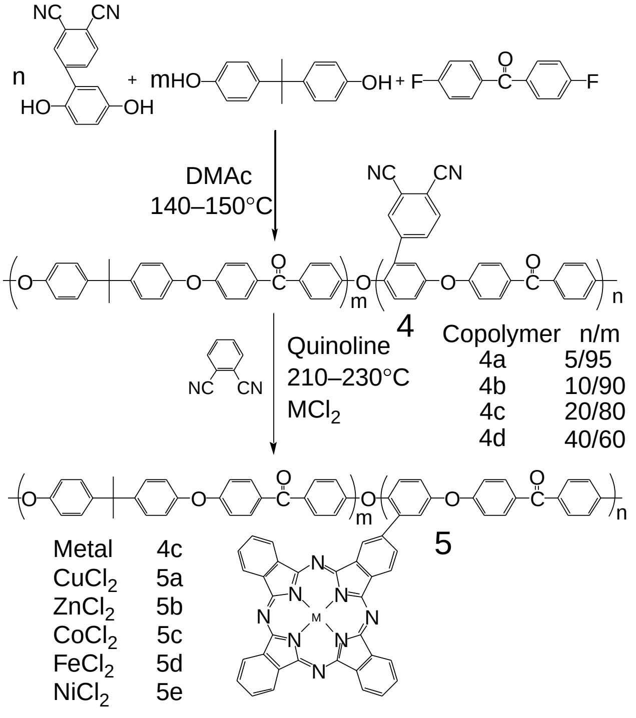
3.1. Synthesis of bisphenol monomer

The bisphenol monomer (compound **3**) was synthesized by the coupling reaction of (3,4-dicyano)phenyldiazonium chloride with 1,4-benzoquinone in the presence of $NaHCO_3$, followed by the reduction of the 1,4-benzoquinone derivative with Zn/HCl (Scheme 1). The structure of compound **3** was confirmed by mass spectrometry, IR, NMR, and elemental analysis. In the IR spectrum, compound **3** shows an absorption band around 1657 cm^{-1} due to the symmetric stretching vibration of carbonyl groups. After reduction, this characteristic absorption disappears, but the characteristic bands of hydroxy groups around 3308 cm^{-1} appear. The compound shows a cyano absorption band around 2240 cm^{-1}. Fig. 2(a) shows the ^{1}H NMR spectrum of bisphenol **3**. The signals at δ 9.37 and 9.00 in the ^{1}H NMR spectrum of bisphenol **3** are assigned to the hydroxyl proton, which could not be observed in the spectrum of the corresponding quinone. The ^{13}C NMR spectrum of bisphenol **3** exhibits 12 peaks, and the peak at δ 117.21 in it is assigned to cyano carbon atoms.

3.2. Synthesis and properties of copolymers of *4a–4d*

The copolymers prepared as shown in the Scheme 2 were characterized by the FTIR and GPC. The yield was about 90%. The IR spectra for the copolymers **4a**–**4d** are presented in Fig. 1. From the spectra, it is evident that the intensity of the –CN band at 2227 cm^{-1} is in the following order: **4a** < **4b** < **4c** < **4d**. The reason for this is as because the mole fraction of –CN contained in **4d** is bigger than those in **4a**–**4c**. The properties of copolymers **4a**–**4d** are listed Table 1. From this table, it is evident that the number average molecular weights of the copolymers vary from 6.08×10^{4} to 1.84×10^{4}. The polydispersities values of the copolymers vary from 1.81 to 1.66. The inherent viscosities values of polymers **4a**–**4d** range from 0.66 to 0.49 dL/g in DMAc.

The glass transition temperatures (T_gs) of the copolymers vary from 156 to 164 °C and are higher than that of BPA-type polyketone. It is also evident from the table that the T_gs of the copolymers increase with increase the content of compound **3**. This is because that the increase in the content of CN as a highly polar group will results in the increase of intermolecular interactions, causing the difficulties in fragment movement. The 5 wt% weight loss temperatures of these copolymers vary from 517 to 482 °C, and the 10 wt% weight loss temperatures vary from 533 to 499 °C, indicating that these copolymers exhibit a good thermal stability.



Scheme 2. Synthesis and properties of copolymers **4** and **5**.

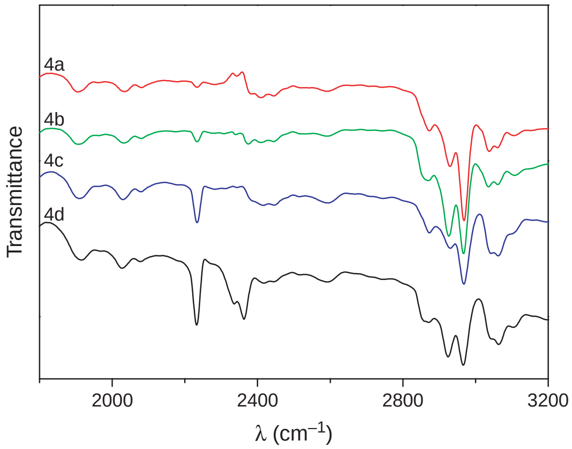


Fig. 1. IR spectra of polymers **4a–4d**.

*3.3. Synthesis and properties of copolymers of **5a–5e***

As depicted in Scheme 2, a metal-complex ring can be formed either intermolecularly or intramolecularly. The formation of intermolecular metal-complex rings can cause cross-linking and insolubilization, which can be avoided by using excessive 1,2-dicyanobenzene followed by extracting with chloroform as described in Section 2. The properties of copolymers **5a–5e** are presented in Table 2. From this table, it can be seen that the number average molecular weights of the copolymers vary from 2.70×10^4 to 2.32×10^4, and the polydispersities values of the copolymers range from 1.77 to 1.71, respectively, which are larger than those of copolymers **4a–4d**. Presumably, the larger polydispersities values of polymers **5** series come from the GPC measurements because of the incorporation of the very bulky metal-containing rings as pendants. Generally, the increase in the rigidity of a polymer backbone leads to the increase in its polydispersity. The inherent viscosities of polymer **5a–5e** range from 0.45 to 0.37 dL/g in DMAc. Also from the same table, we can see that the T_g values vary from 163 to156 °C. These values are almost the same as those of the corresponding copolymers **4a–4d**. The 5 wt% weight loss temperatures vary from 492 to 526 °C, and the 10 wt% weight loss temperatures vary from 519 to 542 °C, which are similar to and higher, respectively, than the corresponding values of copolymer **4c**. These observations indicate that the metals exist in the polymers are responsible for the better thermal stability.

Fig. 2(B) shows the ^{1}H NMR spectrum of copolymer **5b**, in which the signals of protons a and b appear at δ 8.5 and 9.08, respectively, as broad peaks. Because protons a and b are not very close to the core of the large metal-complex ring, the downfield shift effect of the metal-complex ring on the chemical shifts of protons a and b is not significant. However, the ring current affects the conjugated system, so the chemical shifts of protons a and b are high. The signal intensities of protons a and b are weak, because the content of the metal-complex unites is about 13.2% as estimated from the NMR characterization. This value indicates that 66% of the dicyanobenzene groups were converted and incorporated into copolymer **5b**. Fig. 2(C) shows the ^{1}H NMR spectrum of copolymer **5c**, in which the signals of protons a and b appear at δ 8.55 and 8.99, respectively. The content of the metal-complex unites is about 9.2% as estimated from the NMR characterization. This value indicates that 46% of the dicyanobenzene groups were converted and incorporated into copolymer **5c**.

All the copolymers containing metallophthalocyanine were found to be non-birefringent, confirming their amorphous nature. They were found to be soluble in common solvents like DMSO, DMAc, NMP, and $CHCl_3$, etc. It was also found that the copolymers were capable of forming transparent tough films by solution casting or spin-coating from their solutions. These copolymers containing metallophthalocyanine were found to be colored as expected. The colors of polymers **5a–5e** in a chloroform solution are listed in Table 3.

The absorption spectra of copolymers **5a–5e** in a dilute chloroform solution and their films are shown in Fig. 3. It is evident that strong absorption bands in the visible range exist for copolymers **5b** and **5e**, whereas they are moderate for the

Table 1
Properties of copolymers **4a–4d**η

Polymer	η (dL/g)	T_g (°C)	TGA-5% (°C)	TGA-10% (°C)	M_n ($\times10^{-4}$)	Polydispersity
4a	0.66	156	517	533	6.08	1.81
4b	0.59	157	517	530	3.67	1.66
4c	0. 52	159	500	519	2.74	1.71
4d	0.49	164	482	499	1.84	1.79

Table 2
Properties of copolymers **5a–5e**

Polymer	η (dL/g)	T_g (°C)	TGA-5% (°C)	TGA-10% (°C)	M_n (10^{-4})	Polydispersity
5a	0.38	163	494	521	2.70	1.77
5b	0.45	156	492	519	2.48	1.73
5c	0.40	158	520	532	2.62	1.71
5d	0.37	161	520	533	2.32	1.72
5e	0.39	160	526	542	2.44	1.73

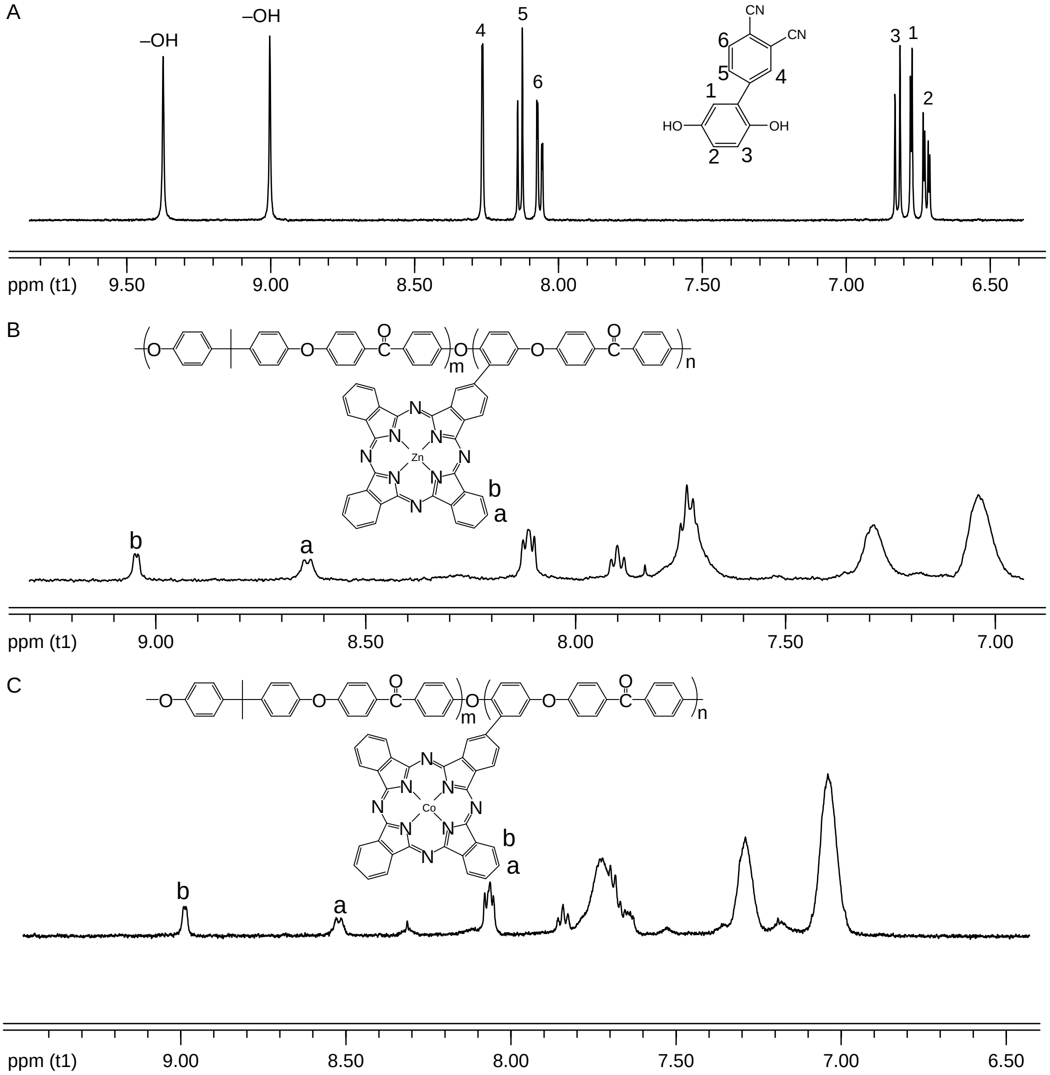


Fig. 2. ^{1}H NMR spectra of monomer (A), polymer **5b** (B) and polymer **5c** (C).

other copolymers. The absorption bands of polymers **5a**–**5e** in a dilute chloroform solution are in a range from 658 to 688 nm and Those of polymers **5a**–**5e** films are in a range from 661 to 699 nm, while the latter are red-shifted compared with the absorption peaks of polymers **5a**–**5e** in a dilute chloroform solution. The maxim values of the absorption of copolymers **5a**–**5e** are presented in Table 3. Fig. 4 shows the fluorescent spectra of polymers **5a**–**5e** in a dilute chloroform solution and those of the films, respectively. As being expected, these polymers are highly fluorescent materials. Polymers **5a**–**5e** give emission at about 450 nm when being excited at about 380 nm.

4. Conclusions

A novel bisphenol, (3,4-dicyano)phenylhydroquinone was prepared via a three-step reaction. On this basis, a series of novel poly(aryl ether ketone) copolymers containing dicyanophenyl groups were prepared was prepared via the reactions of 4,4′-difluorobenzophenone with (3,4-dicyano)phenylhydroquinone and 4,4′-isopropylidenediphenol. In addition, a series of poly(aryl ether ketone)s containing metallophthalocyanine unites were synthesized by the reaction of poly(aryl ether ketone)s containing dicyanophenyl group with excessive amounts of 1,2-dicyanobenzene and the corresponding metal salt in quinoline. All these copolymers were found to have high

Table 3
UV–vis absorption and color of polymers **5a**–**5e**

Polymer	Center metal	λ_{uv} (nm)		Color (in CHCl$_3$)
		Solution	Film	
5a	Cu	688	699	Brown
5b	Zn	684, 720	686	Dark green
5c	Co	672	682	Yellow green
5d	Fe	658	661	Gray green
5e	Ni	665	670	Green

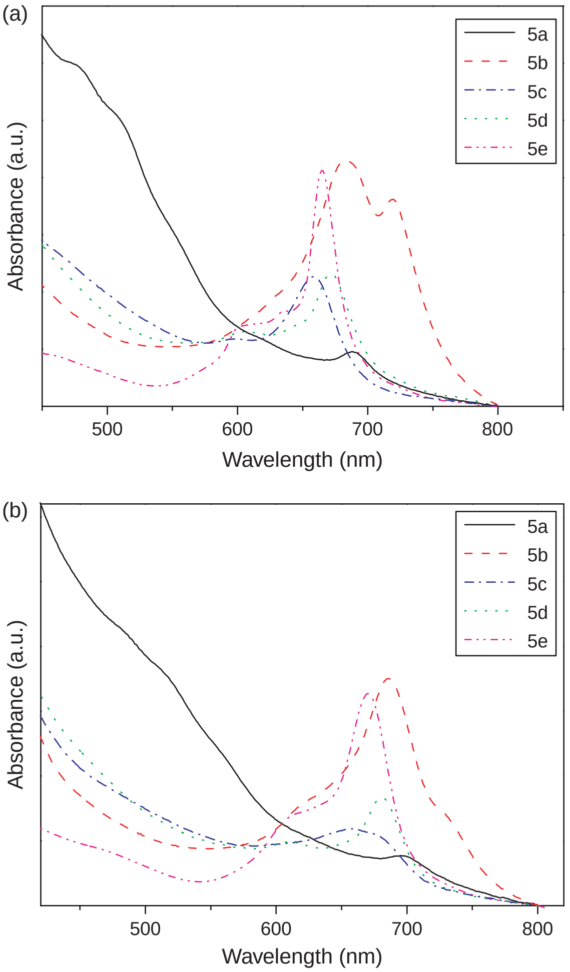


Fig. 3. UV–visible absorption spectra of polymers **5a**–**5e**, A (chloroform solution) and B (film).

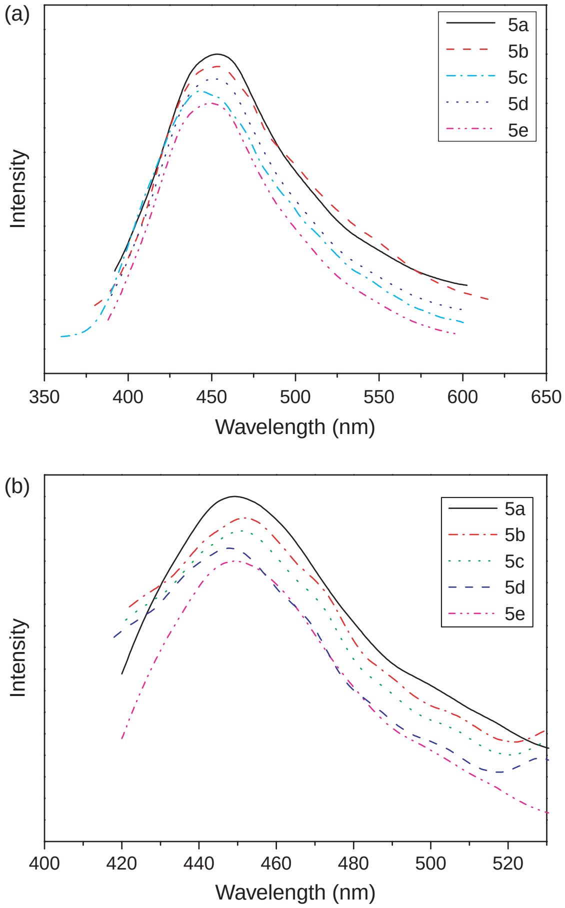


Fig. 4. Fluorescent spectra of polymers **5a**–**5e**, A (chloroform solution) and B (film).

glass transition temperatures and high thermal stability. These copolymers were found to be soluble in common solvents, and to be capable of forming transparent films by solution casting. The copolymers containing metallophthalocyanine unites show strong optical absorption in the visible region, and exhibit strong blue photoluminescence. The polymers can be used as fluorescent materials and electroluminescent materials. Additionally, catalytic activity of the polymers is being studied.

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