Synthesis, luminescence and electrochromism of aromatic poly(amine–amide)s with pendent triphenylamine moieties†

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A new triphenylamine-containing aromatic dicarboxylic acid monomer, *N*,*N*-bis(4-carboxyphenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine (**2**), was synthesized from the amination reaction between 4-aminotriphenylamine and 4-fluorobenzonitrile and subsequent alkaline hydrolysis of the dinitrile intermediate. A series of novel aromatic poly(amine–amide)s with triphenylamine units in the main chain and as the pendent group were prepared from the newly synthesized dicarboxylic acid and various aromatic diamines. These poly(amine–amide)s were amorphous and readily soluble in many organic solvents. All the polymers could be solution-cast into flexible films with good mechanical properties. They had excellent levels of thermal stability associated with high glass-transition temperatures (226–261 °C). These polymers exhibited strong UV–vis absorption bands at 350–365 nm in NMP solution. Their photoluminescence spectra showed maximum bands around 512–543 nm in the green region. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine–amide) **5a** prepared from the dicarboxylic acid monomer **2** with a structurally similar diamine monomer *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine (**4a**) exhibited four reversible oxidation redox couples in acetonitrile solution at $E_{1/2}$ = 0.60, 0.80, 0.97 and 1.13 V, respectively. All the poly(amine–amide)s exhibited excellent reversibility of electrochromic characteristics by continuous five cyclic scans between 0.0 to 1.30 V, with a color change from the original pale yellowish neutral form to the green and then to blue oxidized forms.

Introduction

Triarylamines are an important class of compounds because they are easily oxidized to form stable aminium radical cations. Thus, triarylamines can be building blocks for high-spin polyradicals that have shown ferromagnetic coupling,[1,2] as well as for conductive polymers.[3] Perhaps most commonly, triarylamines have been used as the hole-transport layer in electroluminscent devices.[4–7] A new material with longer life, higher efficiency and an appropriate HOMO energy level is in increasing demand and most of the charge transporting materials are low molecular weight compounds; of these, *N*,*N*,*N*′,*N*′-tetraryl-1,4-phenylenediamine, *N*,*N*,*N*′,*N*′-tetraryl-benzidine and triphenylamine (TPA) derivatives have been extensively investigated because of their high charge mobility and electrochromism.[8–14] The main disadvantage, which often makes application difficult, is their insufficient morphological stability and susceptibility to crystallization or phase separation. To solve this problem, attempts to introduce TPA units into the main or side chain of the polymer backbone were undertaken intensively, and some important results have been obtained.[15–24] One of the perceived advantages is that polymer films can be more easily deposited over a larger area and they are often flexible. Furthermore, prevention of crystallization and phase separation may improve the device performance. The uses of polymeric materials also provide the possibility for various chemical design and modifications.[25]

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong hydrogen bonding results in high melting or glass-transition temperatures (T_g's) and limited solubility in most organic solvents.[26,27] These properties make them generally intractable or difficult to process, thus restricting their applications. To overcome such a difficulty, polymer structure modification becomes necessary. Recently, we have reported the synthesis of soluble aromatic polyamides and polyimides bearing triphenylamine units in the main chain based on *N*,*N*′-bis(4-aminophenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine,[28,29] *N*,*N*′-bis(4-carboxyphenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine,[30] 2,4-diaminotriphenylamine,[31] and *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine,[32,33] respectively. Because of the incorporation of bulky, three-dimensional triphenylamine units along the polymer backbone, all the polymers were amorphous, had good solubility in many aprotic solvents, and exhibited excellent thin-film-forming capability. Imai *et al.* reported that the charge injection and electroluminescent efficiency were improved remarkably by the incorporation of the hole-transporting polyimide containing a triphenylamine unit in the backbone.[34]

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† Electronic supplementary information (ESI) available: Synthesis and discussion of monomer starting materials and characterization Figs. S1–4 (IR and NMR spectra). Color Figs. 3, 6–8 showing PL and electrochromic properties of the polymers. See http://www.rsc.org/suppdata/jm/b4/b419183h/

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Therefore, the introduction of triphenylamine units into aromatic polyamide and polyimide backbones would be expected to be a potential structural approach for not only increasing solubility without sacrificing high thermal stability but also allowing them to be used as potential hole-transporting materials. Nevertheless, little is known to date about the preparation, electrochemical and electrochromic properties of aromatic polyamides or polyimides having *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine unit in the main backbone. The only examples are poly(amine–imide)s[32] and poly(amine–amide)s[33] derived from *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine. As a continuation of these studies, we seek to create redox arrays designed for controlling the hole-transport and electrochromic properties of aromatic polyamides by adjoining N-based redox functions of different oxidation potential. In the present article, we designed a novel class of *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine-containing poly(amine–amide)s with mixed redox pendent triphenylamine groups of varied oxidation potential to elucidate the effect of their corresponding radical cations on the electrochromic behavior of the poly(amine–amide)s derived from the new dicarboxylic acid, *N*,*N*-bis(4-carboxyphenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine (**2**). The general properties such as solubility, crystallinity, thermal and mechanical properties are reported. The electrochemical, electrochromic and photoluminescence properties of these polymers prepared by casting solution onto an indium tin oxide (ITO)-coated glass substrate are also investigated and compared with those of structurally related ones from 4,4′-dicarboxytriphenylamine (**3**).

Experimental

Materials

According to well-known chemistry,[35–37] 4-aminotriphenylamine (mp = 148–149 °C) was prepared by the aromatic nucleophilic amination of 4-nitrofluorobenzene and diphenylamine in *N*,*N*-dimethylformamide (DMF) in the presence of sodium hydride, followed by reduction by means of hydrazine and Pd/C in refluxing ethanol. 4,4′-Dicarboxytriphenylamine (**3**) (mp = 313–315 °C; lit.[38] 308–310 °C) was synthesized by the caesium fluoride-assisted condensation of aniline with 4-fluorobenzonitrile, followed by alkaline hydrolysis of the intermediate dinitrile compound according to a reported procedure.[38] *N*,*N*-Bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine[32] (**4a**; mp = 245–247 °C) and 4,4′-diaminotriphenylamine[39] (**4b**; mp = 186–187 °C) were synthesized by the nucleophilic fluoro-displacement reaction of 4-fluoronitrobenzene with 4-aminotriphenylamine and aniline, respectively, followed by palladium-catalyzed hydrazine reduction. 4-Fluorobenzonitrile (Tokyo Chemical Industries), sodium hydride (95%, dry, Aldrich), potassium hydroxide (Tedia) were used as received. *N*,*N*-Dimethylacetamide (DMAc) (Tedia), *N*,*N*-dimethylformamide (DMF) (Acros), dimethyl sulfoxide (DMSO) (Tedia), *N*-methyl-2-pyrrolidinone (NMP) (Tedia), pyridine (Py) (Tedia), triphenyl phosphite (TPP) (Acros) were used without further purification. Commercially available aromatic diamines such as *p*-phenylenediamine (**4c**) (TCI), *m*-phenylenediamine (**4d**) (TCI), and 4,4′-oxydianiline (**4e**) (TCI) were used as received. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) was obtained from Acros and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Preparation of poly(amine–amide)s

The synthesis of poly(amine–amide) **5a** is used as an example to illustrate the general synthetic route. The typical procedure is as follows. A mixture of 0.626 g (1.25 mmol) of the triphenylamine-based dicarboxylic acid monomer **2**, 0.553 g (1.25 mmol) of *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine (**4a**), 0.15 g of calcium chloride, 0.9 mL of TPP, 0.6 mL of pyridine, and 2.5 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried at 150 °C for 15 h *in vacuo*. Precipitations from NMP into methanol were carried out twice for further purification. The inherent viscosity of the obtained poly(amine–amide) **5a** was 0.80 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} in NMP at 30 °C. The IR spectrum of **5a** (film) exhibited characteristic amide absorption bands at 3316 (N–H stretching), 1668 cm^{-1} (amide carbonyl). Anal. Calcd For $(C_{62}H_{46}N_6O_2)_n$ $(907.07)_n$: C, 82.10%; H, 5.11%; N, 9.27%. Found: C, 81.40%; H, 5.27%; N, 9.16%. Other poly(amine–amide)s were prepared by an analogous procedure.

Film preparation

A solution of polymer was made by dissolving about 0.6 g of the poly(amine–amide) sample in 10 mL of NMP. The homogeneous solution was poured into a 9 cm glass Petri dish, which was placed in a 90 °C oven overnight to remove most of the solvent. The cast film was then released from the glass substrate and was further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 50–60 μm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests and thermal analyses.

Measurements

Infrared spectra were recorded on a Perkin Elmer RXI FT-IR spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500 MHz FT-NMR system. The X-ray crystallographic data were collected on an Enraf-Norius FR 590 CAD-4 diffractometer. Elemental analyses were run in an Elementar VarioEL-III. The inherent viscosities were determined at 0.5 g dL^{-1} concentration using a Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements of the polymer films were performed at room temperature (*ca.* 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA) with a graphite monochromator, using nickel-filtered CuKα radiation. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm width, 6 cm length), and an average of at least three replicates was used. Thermogravimetric 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 = 40 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. DSC analyses were performed on a Perkin Elmer Pyris 1 DSC at a scan rate of 20 °C min^{-1} in flowing nitrogen (20 cm^3 min^{-1}). 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^{-1} with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperatures of probe displacement on the TMA traces. Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was performed 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. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. The spectroelectrochemical cell was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode and a Ag/AgCl reference electrode. Absorption spectra were measured with a HP 8453 UV–visible spectrophotometer. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer.

Results and discussion

Polymer synthesis

A series of novel aromatic poly(amine–amide)s **5a–e** having the triphenylamine unit in the main chain and as the pendent group were prepared from the newly synthesized dicarboxylic acid **2** (Fig. 1 and Scheme 1) and various aromatic diamines **4a–e** by the phosphorylation polycondensation reaction[40] using TPP and pyridine as condensing agents (Scheme 2). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured with stirring into methanol. These poly(amine–amide)s were obtained in almost quantitative yields, with inherent viscosity values in the range of 0.59–1.04 dL g^{-1}. The formation of poly(amine–amide)s was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polymers are listed in Table 1. Fig. 2 shows a typical IR spectrum of poly(amine–amide) **5a**. They exhibited characteristic IR absorption bands of the amide group around 3316 (N–H stretching) and 1668 cm^{-1} (amide carbonyl). For a comparative study, a series of referenced poly(amine–amide)s **6a–e** were also synthesized from 4,4′-dicarboxytriphenylamine (**3**) and corresponding diamines **4a–e**.

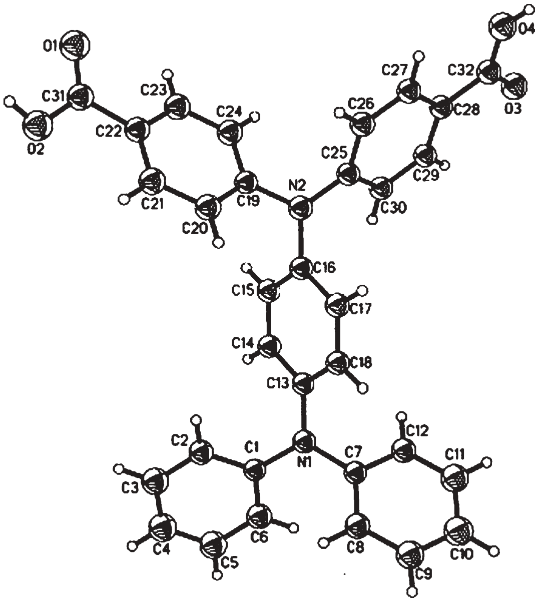
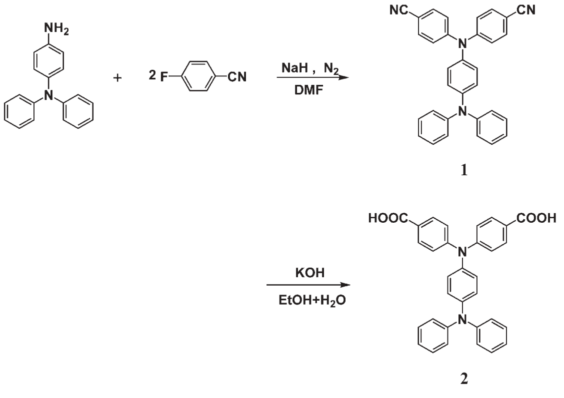
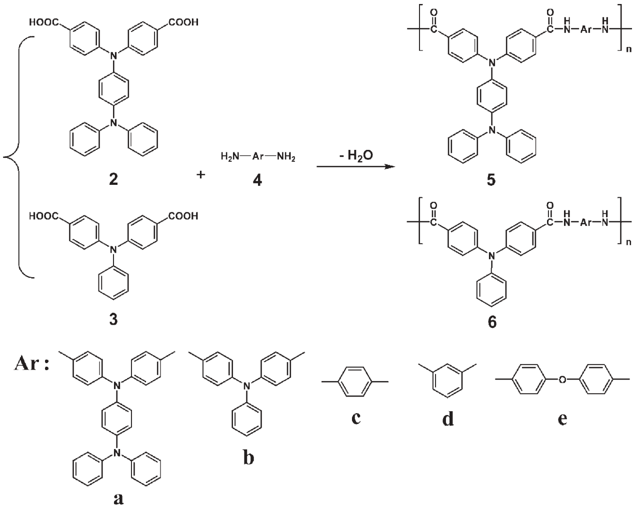


Fig. 1 Molecular structure of dicarboxylic acid **2** by single crystal X-ray analysis.



Scheme 1



Scheme 2

Table 1 Inherent viscosity and elemental analysis of poly(amine–amide)s

Poly(amine–amide)s		Elemental analysis (%) of poly(amine–amide)s				
Code	η_{inh}[a]/ dL g^{-1}	Formula (molecuar weight)		C	H	N
5a	0.80	$(C_{62}H_{46}N_6O_2)_n$	Calcd	82.10	5.11	9.27
		$(907.07)_n$	Found	81.40	5.27	9.16
5b	0.39	$(C_{50}H_{37}N_5O_2)_n$	Calcd	81.17	5.04	9.47
		$(739.86)_n$	Found	79.71	5.13	9.07
5c	0.70	$(C_{38}H_{28}N_4O_2)_n$	Calcd	79.70	4.93	9.78
		$(572.65)_n$	Found	77.71	5.13	9.51
5d	0.96[b]	$(C_{38}H_{28}N_4O_2)_n$	Calcd	79.70	4.93	9.78
		$(572.65)_n$	Found	76.94	5.07	9.52
5e	1.04	$(C_{44}H_{32}N_4O_3)_n$	Calcd	79.50	4.85	8.43
		$(664.75)_n$	Found	77.55	5.03	8.54
6a	0.57	$(C_{50}H_{37}N_5O_2)_n$	Calcd	81.17	5.04	9.47
		$(739.86)_n$	Found	79.04	5.23	9.13
6b	0.53	$(C_{38}H_{28}N_4O_2)_n$	Calcd	79.70	4.93	9.78
		$(572.65)_n$	Found	77.85	5.11	9.29
6c	0.76	$(C_{26}H_{19}N_3O_2)_n$	Calcd	77.02	4.72	10.36
		$(405.45)_n$	Found	74.42	5.02	10.06
6d	0.45	$(C_{26}H_{19}N_3O_2)_n$	Calcd	77.02	4.72	10.36
		$(405.45)_n$	Found	73.55	5.07	10.29
6e	1.75	$(C_{32}H_{23}N_3O_3)_n$	Calcd	77.25	4.66	8.45
		$(497.54)_n$	Found	74.25	4.87	8.43

[a] Measured at a polymer concentration of 0.5 g dL^{-1} in NMP at 30 °C [b] Measured at polymer concentration of 0.5 g dL^{-1} in NMP contain 5% LiCl.

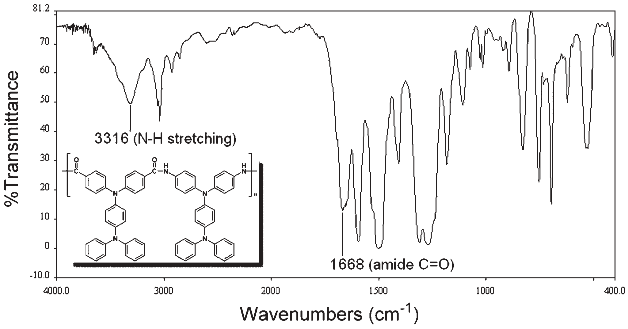


Fig. 2 IR spectrum (film) of poly(amine–amide) **5a**

Basic characterization

The wide-angle X-ray diffraction studies of the poly(amine–amide)s indicated that these polymers were essentially amorphous. The qualitative solubility properties of the poly(amine–amide)s are presented in Table 2, and most of these polymers exhibited good solubility to highly polar organic solvents due to the introduction of the three-dimensional triphenylamine core in the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin- or dip-coating processes. It is worth noting that polymer **5d** formed an opaque film *via* solution casting from NMP and showed less solubility. The reason is not apparent to us at this time. Except for **5d**, these polymers could afford transparent, flexible and tough films and they were subjected to tensile testing. As shown in Table 3, the tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 66–110 MPa, 9–26% and 1.6–2.3 GPa, respectively.

Table 2 Solubility[a] of aromatic poly(amine–amide)s

	Solvent						
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Chloroform
5a	+	+	+h	+h	+h	—	—
5b	+	+	+	+h	+h	—	—
5c	+	+	+	+	+	—	—
5d	±	—	—	—	±	—	—
5e	+	±	±	±	±	—	—
6a	+	+	+	+h	+h	±	—
6b	+	+	+h	+h	+	—	—
6c	+	±	±	±	±	—	—
6d	+	+	+h	+h	+h	—	—
6e	+	±	±	+h	±	—	—

[a] Solubility: +, soluble at room temperature; +h, soluble on heating; ±, partially soluble or swelling; −, insoluble even on heating.

Table 3 Mechanical properties of poly(amine–amide) films

Polymer	Tensile strength/MPa	Elongation at break (%)	Initial modulus/GPa
5a	74	22	1.7
5b	68	11	1.6
5c	78	23	2.0
5e	110	8	2.3
6a	73	24	1.8
6b	72	8	1.8
6c	73	26	1.7
6d	96	10	2.0
6e	66	9	1.8

The thermal properties of all the poly(amine–amide)s were investigated by TGA, DSC and TMA. The results are summarized Table 4. All the polymers exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen. The 10% weight-loss temperatures of the polyamides in nitrogen and air were recorded in the range of 454–568 and 468–578 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 55% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This

Table 4 Thermal properties of aromatic poly(amine–amide)s

			T_d at 5% weight loss/°C[c]		T_d at 10% weight loss°C[c]		
Polymer	T_g/ °C[a]	T_s/ °C[b]	N_2	Air	N_2	Air	Char yield (wt.%)[d]
5a	257	257	510	518	557	578	59
5b	261	261	505	488	568	570	66
5c	257	250	464	458	526	534	69
5d	260	255	505	476	545	511	55
5e	226	215	464	445	522	514	68
6a	268	268	471	475	534	552	68
6b	277	274	463	453	530	528	69
6c	294	295	450	457	496	513	70
6d	265	262	428	423	454	468	69
6e	256	251	442	445	495	483	67

[a] Midpoint temperature of baseline shift on the DSC heating trace (rate 20 °C min^{-1}) of the sample after heating at 300 °C for 1 h. [b] Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C min^{-1}. [c] Decomposition temperature, recorded *via* TGA at a heating rate of 20 °C min^{-1} and a gas-flow rate of 40 cm^3 min^{-1}. [d] Residual weight percentage at 800 °C in nitrogen.

result also supports the amorphous nature of these triphenylamine-containing polymers. The T_g's of all the polymers were measured to be in the range of 226–294 °C by DSC. The values are substantially higher than that of 4,4′-bis[*N*,*N*-(*m*-tolyl)-phenylamino]biphenyl (TPD) (63 °C), indicating that the use of these polymers may greatly improve the device durability, which relates to the T_g's of the materials as reported by Tokito *et al.*[41,42] The softening temperatures (T_s) of the polymer film samples were determined by the TMA method with a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. In all cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. When compared with the analogous poly(amine–amide)s **6**, the **5** series of poly(amine–amide)s showed a slightly decreased T_g and T_s that may be attributed to the increased conformational flexibility or free volume caused by the introduction of the bulky pendent triphenylamine group in the repeat unit.

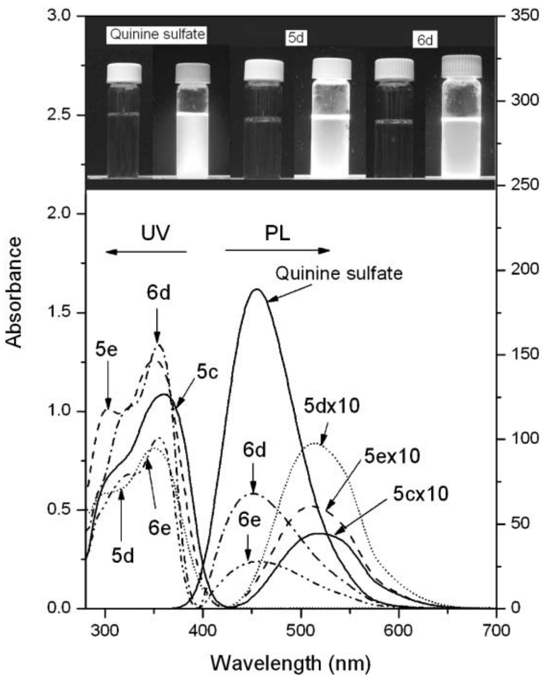


Fig. 3 Absorptions and PL spectra of poly(amine–amide)s with a concentration of NMP (5 mg mL^{-1}). Quinine sulfate dissolved in 1 N H_2SO_4 (aq.) with a concentration of (7.8 μg mL^{-1}), assuming ϕPL of 0.55.

Optical and electrochemical properties

The optical and electrochemical behavior of the poly(amine–amide)s were investigated by UV–vis, photoluminescence spectroscopy, and cyclic voltammetry. The results are summarized in Table 5. The UV–vis absorption spectra of these polymers exhibited strong absorption bands at 350–365 nm in NMP solution, which are assignable to the π–π* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Fig. 3 shows the UV–vis absorption and photoluminescence spectra of poly(amine–amide)s **5c–e**, **6d** and **6e** for comparison. In the solution photoluminescence spectra, **5c–e** emitted in the green region (512–519 nm), while **6d** and **6e** emitted in the blue region (451–469 nm). Compared to the polymer **5d** exhibiting an emission peak at 513 nm, the corresponding polymer **6d** showed blue-shifted emission spectrum with the maxima peak at around 451 nm. Apparently the emission in long wavelength region for the **5** series was due to the existence of the pendent triphenylamine groups, which resulted in a lower HOMO energy level and decreased the energy gap between HOMO and LOMO. Comparing with the corresponding PL intensity of poly(amine–amide)s, the **6** series is relatively greater than that of the **5** series. This phenomenon possibly could be attributed to the Stokes shift being clearly greater for the **5** series and this results in the lower emission quantum yield than the **6** series due to the greater number of conformations and a higher rate of radiationless decay. The polymer films were measured for optical transparency using UV–vis spectroscopy, and the cutoff wavelengths (absorption edge; λ_0) were in the range of 412–462 nm. The electrochemical behavior of the **5** and **6** series poly(amine–amide)s was investigated by cyclic voltammetry performed for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for poly(amine–amide) **5a** and **5c** are shown in Fig. 4 and Fig. 5, respectively. There are four reversible

Table 5 Optical and electrochemical properties for the aromatic poly(amine–amide)s

Code	$\lambda_{abs,max}$/ nm[a]	$\lambda_{abs,onset}$/ nm[a]	λ_{PL}/ nm[b]	λ_0/ nm[c]	Oxidation/V (*vs.* Ag/AgCl) First	Second	Third	Fourth	HOMO–LUMO gap[e]/eV	HOMO[f]/ eV	LUMO[g]eV
5a	358 (353)	417 (428)	543 (526)	464	0.60	0.80	0.97	1.13	2.90	4.96	2.06
5b	356 (355)	412 (421)	525 (516)	458	0.80	1.14	—	—	2.95	5.16	2.21
5c	361 (358)	406 (421)	519 (515)	454	0.77	1.13	—	—	2.95	5.13	2.18
5d	350 (357)	403 (416)	513 (513)	—	0.78	1.14	—	—	2.98	5.14	2.16
5e	350 (355)	398 (414)	512 (509)	448	0.77	1.14	—	—	3.00	5.13	2.13
6a	363 (359)	407 (417)	537 (514)	462	0.59	0.96	—	—	2.97	4.95	1.98
6b	363 (359)	404 (413)	518 (497)	446	0.83	(1.19)[d]	—	—	3.00	5.19	2.19
6c	365 (355)	392 (403)	469 (454)	422	(1.22)[d]	—	—	—	3.08	5.58	2.50
6d	354 (361)	386 (401)	451 (453)	429	(1.14)[d]	—	—	—	3.09	5.50	2.41
6e	354 (355)	385 (404)	458 (452)	412	(1.20)[d]	—	—	—	3.07	5.56	2.49

[a] UV–vis absorption measurements in NMP (0.02 mg mL^{-1}) at room temperature, values in parentheses are polymer thin films. [b] PL spectra measurements in NMP (5 mg mL^{-1}) at room temperature, values in parentheses are polymer thin films. [c] The cutoff wavelengths (λ_0) from the transmission UV–vis absorption spectra of polymer films. [d] Irreversible peak potential ($E_{p,a}$). [e] The data were calculated in film state by the equation: gap = 1240/λ_{onset}. [f] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). [g] LUMO = HOMO − gap.

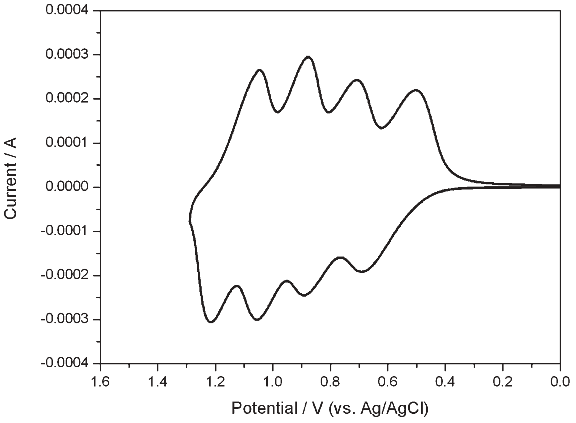


Fig. 4 Cyclic voltammogram of poly(amine–amide) **5a** film onto an indium tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V s^{-1}.

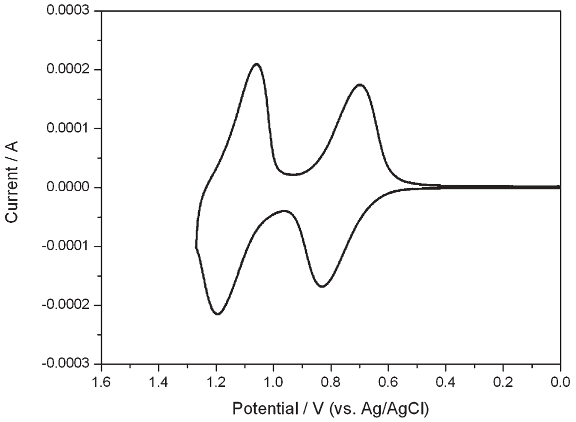


Fig. 5 Cyclic voltammogram of poly(amine–amide) **5c** film onto an indium tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V s^{-1}

oxidation redox couples for poly(amine–amide) **5a** at $E_{1/2}$ = 0.60, 0.80, 0.97 and 1.13 V corresponding to successive one-electron removal from the nitrogen atoms at both *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine structures in each repeating unit to yield two stable delocalized radical cations, poly(amine–amide)$^+$ and poly(amine–amide)$^{3+}$, and two stable quinonoid-type dications, poly(amine–amide)$^{2+}$ and poly(amine–amide)$^{4+}$, respectively.[43] Both triarylamine centers at each *N*,*N*,*N*′,*N*′-tetraphenyl-1,4-phenylenediamine structures of repeating unit are strongly coupled by the fact that the redox couple separations are 370 mV (0.97–0.60 V) and 330 mV (1.13–0.80 V), respectively, which are larger than the statistical value for non-interacting centers, where the separation of the first and the second oxidation redox couple is 35.6 mV.[44] Because of the good stability of the films and excellent adhesion between the polymer and ITO substrate, the poly(amine–amide)s **5a** exhibited great reversibility of electrochromic characteristics by continuous five cyclic scans between 0.0 to 1.30 V, changing color from the original pale yellowish to green, and then to blue. Comparing the oxidation potential data, it was found that poly(amine–amide) **5d** with pendent triphenylamine groups (0.78 V) is much easier oxidized than poly(amine–amide) **6d** without pendent triphenylamine groups (1.14 V). The first electron removal for poly(amine–amide) **5d** is believed to occur at the N atom on the pendent triphenylamine unit, which is more electron-rich than the N atom on the main-chain triphenylamine group surrounded by two phenyl groups with amide linkages. The energy of the HOMO and LUMO levels of the investigated poly(amine–amide)s can be determined from the oxidation half-wave potentials and the onset absorption wavelength and the results are listed in Table 5. For example, the oxidation half-wave potential for poly(amine–amide) **5c** has been determined as 0.77 V *vs* Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ is 0.44 V *vs*. Ag/AgCl in CH_3CN. Assuming that the HOMO energy for the Fc/Fc^+ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for poly(amine–amide) **5c** has been evaluated to be 5.13 eV.

Electrochromic characteristics

Electrochromism of the thin films from poly(amine–amide)s was determined by optically transparent thin-layer electrode (OTTLE) coupled with a UV–vis spectroscopy. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of poly(amine–amide) **5a** and **5c** are shown as Figs. 6–8. When the applied potentials increased positively from 0 to 0.73, 0.93, 1.09, 1.26 V, respectively, corresponding to the first, second, third and fourth electron oxidation, the peak of characteristic absorbance at 342 nm for neutral form poly(amine–amide) **5a** decreased gradually, while four new bands grew up at 987, 938, 730 and 714 nm, respectively. The new spectral patterns were assigned as those of the cationic radical poly(amine–amide)$^+$, poly(amine–amide)$^{2+}$, poly(amine–amide)$^{3+}$, and poly(amine–amide)$^{4+}$, respectively, the products obtained by electron removal from the lone pair of nitrogen atom on different two *p*-phenylenediamine structures. According to the electron density among the four nitrogen atoms on different two *p*-phenylenediamine structures in each repeating unit, the anodic oxidation pathway of poly(amine–amide) **5a** was postulated as in Scheme 3.

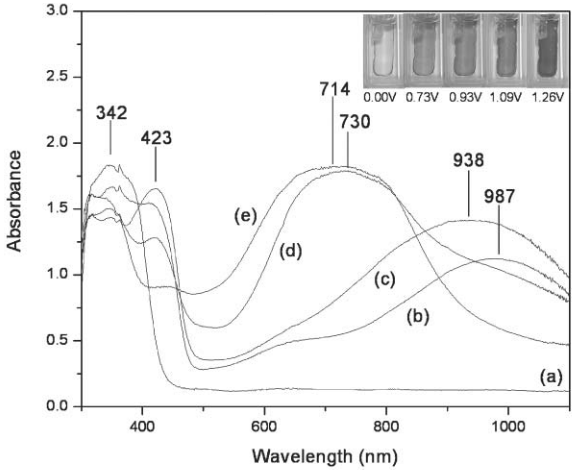


Fig. 6 Electrochromic behavior of poly(amine–amide) **5a** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0 (b) 0.73 (c) 0.93 (d) 1.09 (e) 1.26 V.

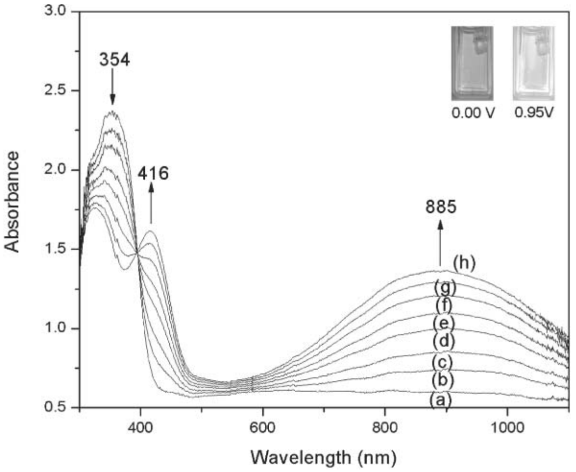


Fig. 7 Electrochromic behavior of poly(amine–amide) **5c** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0 (b) 0.70 (c) 0.73 (d) 0.77 (e) 0.80 (f) 0.83 (g) 0.85 (h) 0.95 V.

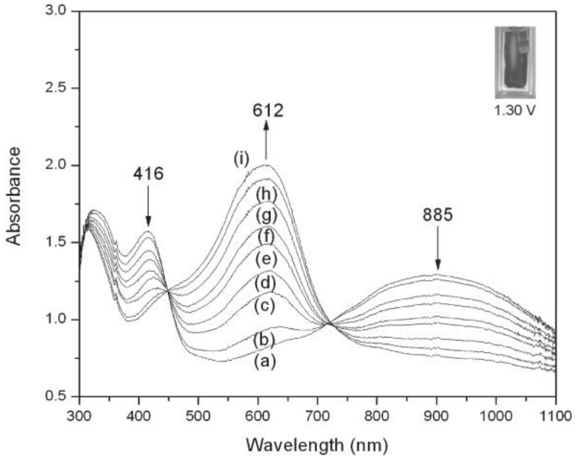
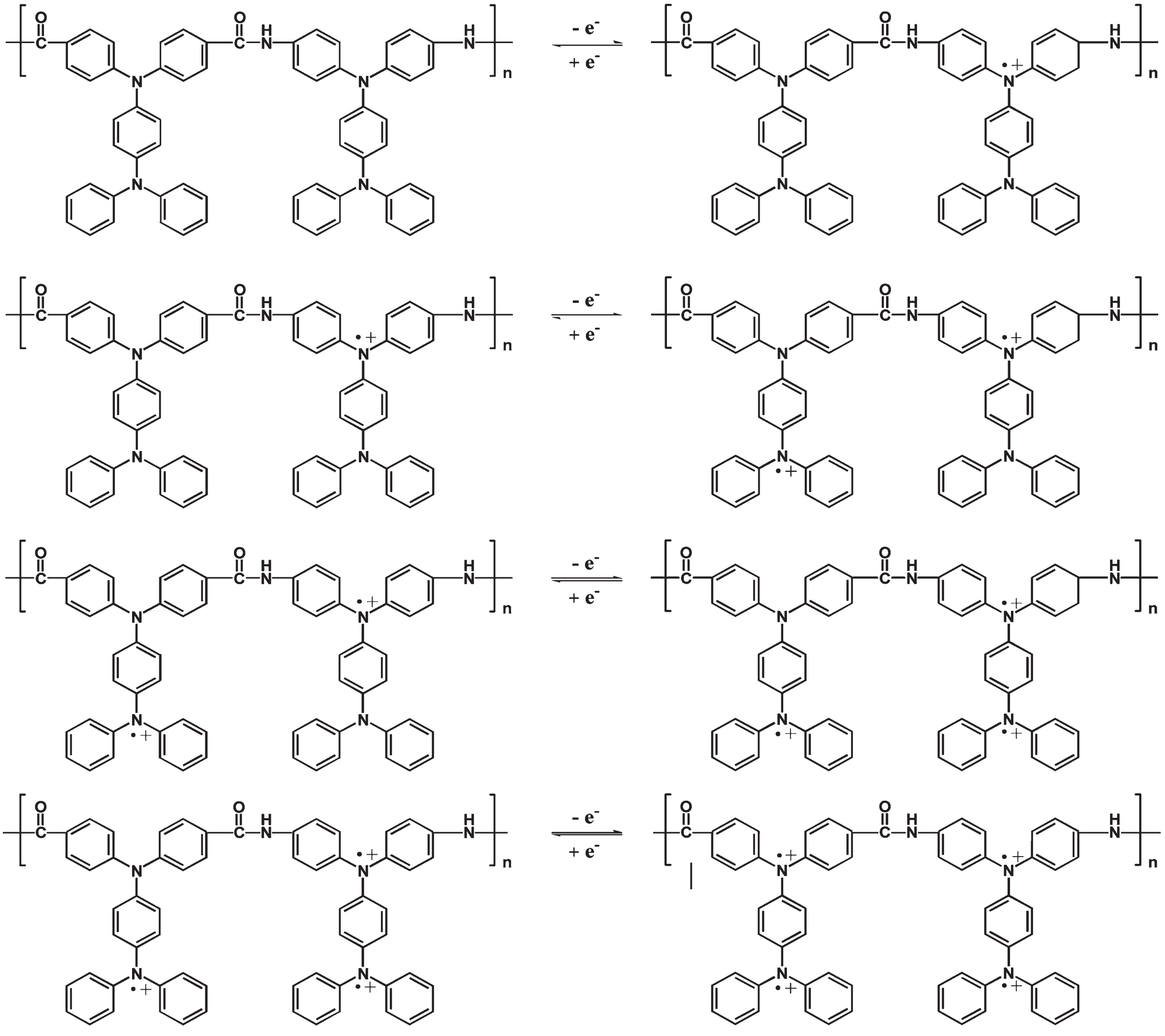


Fig. 8 Electrochromic behavior of poly(amine–amide) **5c** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 1.01 (b) 1.05 (c) 1.07 (d) 1.10 (e) 1.13 (f) 1.16 (g) 1.19 (h) 1.25(i) 1.30 V.



Scheme 3

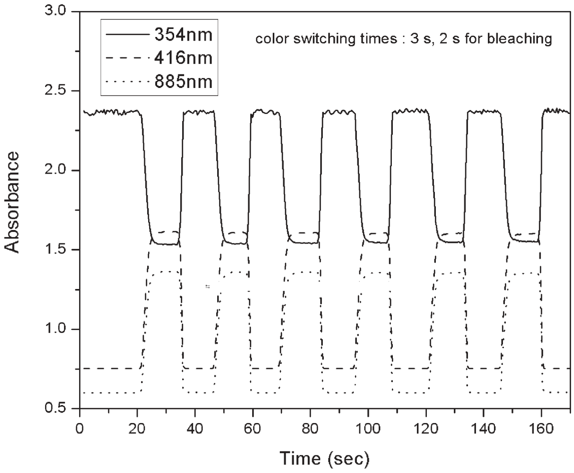


Fig. 9 Potential step absorptometry of poly(amine–amide) **5c** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V 0.95 V).

Meanwhile, the complementary color of the **5a** film changed from the original pale yellowish to green, and then to blue (as shown in Fig. 6) due to different oxidation state. The electrochromic characteristics of poly(amine–amide) **5c** was also shown in Fig. 7 and Fig. 8. Thus, this will be a good approach for facile color tuning of the electrochromic behaviors by attaching triphenylamine units to polymer main chain and/or as pendent group.

The color switching times were estimated by applying a potential step, and the absorbance profiles were followed. The switching time was defined as the time that was required to reach 90% of the full change in absorbance after switching potential. Thin films from poly(amine–amide) **5c** would require 3 s at 0.95 V for switching absorbance at 416 and 885 nm and 2 s for bleaching (Fig. 9). When the potential was set at 1.30 V, thin films from poly(amine–amide) **5c** would require almost 4 s for coloration at 612 nm and 2 s for bleaching (Fig. 10). Continuous five cyclic scans between 0.0 to 1.40 V, the polymer films still exhibited excellent stability of electrochromic characteristics.

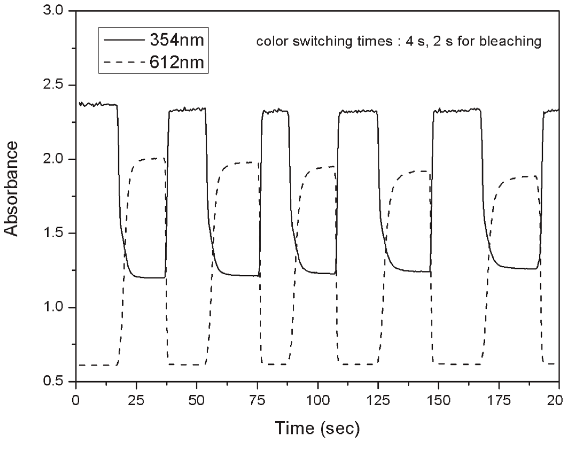


Fig. 10 Potential step absorptometry of poly(amine–amide) **5c** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V 1.30 V).

Conclusions

A series of new high-molecular weight poly(amine–amide)s **5a–e** having triphenylamine units both in polymer main chain and pendent group have been readily prepared from the aromatic dicarboxylic acid, *N*,*N*-bis(4-carboxyphenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine and various aromatic diamines. Attaching bulky and inherently electron-donating triphenylamine units to the polymer main chain and/or as pendent group, not only could be a good approach to facile color tuning of the electrochromic behaviors due to the oxidation potentials being adjusted, but also disrupts the coplanarity of aromatic units in chain packing, which increases the between-chains spaces or free volume, thus most of the polymers were amorphous with good solubility in many polar aprotic solvents and exhibited excellent thin-film-forming ability. In addition to high T_g or T_s values, good thermal stability, and mechanical properties, all the obtained poly(amine–amide)s also revealed excellent stability of electrochromic characteristics by the electrochemical and spectroelectrochemical methods, changing color from the original pale yellowish to green, and then to blue. Thus, these novel triphenylamine-containing poly(amine–amide)s may find applications in electroluminscent devices as hole-transporting layer and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stability.

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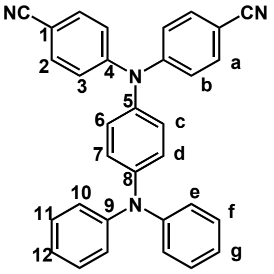
Synthesis, luminescence, and electrochromism of aromatic poly(amine-amide)s with pendant triphenylamine moieties

Supporting Information

Synthesis of monomer:

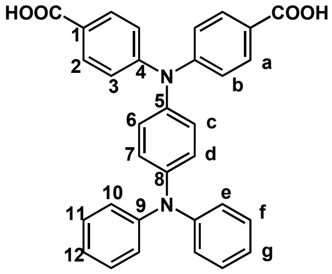
N,N-Bis(4-cyanophenyl)-*N',N'*-diphenyl-1,4-phenylenediamine (1)

A mixture of 0.98 g (0.039 mol) of sodium hydride and 50 mL of DMSO was stirred at room temperature. To the mixture, 5.00 g (0.019 mol) of 4-aminotriphenylamine and 4.89 g (0.04 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 140 °C for 10 h under nitrogen and then precipitated into 700 mL of cold water. Recrystallization from toluene yielded 2.93 g of the desired dinitrile compound **1** as yellowish needles in 33 % yield; mp = 192–194 °C measured by DSC at 10 ^{o}C/min. IR (KBr): 2219 cm^{-1} (C≡N). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.54 (d, J = 8.7 Hz, 4H, H_a), 7.27 (t, J = 7.9 Hz, 2H, H_f), 7.15 (d, J = 8.7 Hz, 2H, H_c), 7.05 (d, J = 8.7 Hz, 4H, H_b), 7.02 ~ 6.97 (m, 8H, $H_d + H_e + H_g$). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 148.86 (C^4), 147.68 (C^9), 142.33 (C^5), 136.55 (C^8), 133.95 (C^2), 129.76 (C^{11}), 126.14 (C^7), 123.28 (C^{10}), 122.78 (C^{12}), 121.85 (C^6), 120.43 (-CN), 114.61 (C^3), 99.01 (C^1). Anal. Calcd for $C_{32}H_{22}N_4$ (462.54): C, 83.09 %; H, 4.79 %; N, 12.11 %. Found: C, 83.35 %; H, 4.72 %; N, 11.93 %.



_N,N_-Bis(4-carboxyphenyl)-_N’,N’_-diphenyl-1,4-phenylenediamine (2)

A mixture of 9.26 g of potassium hydroxide and 4.88 g of the obtained dinitrile compound **1** in 30 mL of ethanol and 30 mL of distillated water was stirred at approximately 100 °C until no further ammonia was generated. The time taken to reach this stage was about 4–5 days. The solution was cooled, and the pH value was adjusted by dilute hydrochloric acid to near 3. The crude precipitate was washed thoroughly with water and recrystallized from acetonitrile/methanol, and dried to give 4.18 g (yield: 76%) of yellowish diacid product; mp = 274–277 °C measured by DSC at 10°C/min. IR (KBr): 1674 (C=O), 2700–3400 cm^{-1}(O-H). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 12.66 (s, 2H, -COOH), 7.86 (d, $J = 8.7$ Hz, 4H, H$_a$), 7.29 (t, $J = 7.8$ Hz, 4H, H$_f$), 7.06 (d, $J = 8.7$ Hz, 4H, H$_b$), 7.04 (t, $J = 7.8$ Hz, 2H, H$_g$), 7.03 (d, $J = 7.9$ Hz, 4H, H$_e$), 7.01 (d, $J = 8.8$ Hz, 2H, H$_c$), 6.95 (d, $J = 8.8$ Hz, 2H, H$_d$). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 167.29 (C=O), 150.67 (C^4), 147.26 (C^9), 145.17 (C^5), 139.96 (C^8), 131.30 (C^2), 129.92 (C^{11}), 128.10 (C^1), 124.64 (C^7), 124.53 (C^6), 124.39 (C^{10}), 123.64 (C^{12}), 122.02 (C^3). Anal. Calcd for $C_{32}H_{24}N_2O_4$ (500.53): C, 76.78%; H, 4.83%; N, 5.60%. Found: C, 76.74 %; H, 4.76 %; N, 5.67 %. Crystal data: Yellowish crystal grown during the slow crystallization in acetonitrile, 0.30 x 0.25 x 0.20 mm, Triclinic P$\underline{1}$ with $a = 10.3279(2)$, $b = 16.7871(2)$, $c = 17.1973(2)$ Å; $\alpha = 105.8920(10)^o$, $\beta = 105.8580(10)^o$, $\gamma = 104.2400(10)^o$ where density of crystal Dc = 1.285 Mg/m^3 for $Z = 4$ and $V = 2587.35(7)$ Å^3.



Results and Discussion

Monomer Synthesis

The new aromatic dicarboxylic acid having bulky pendent triphenylamine group, *N,N*-bis(4-carboxyphenyl)-*N',N'*-diphenyl-1,4-phenylene- diamine (**2**), was successfully synthesized by the condensation of 4-aminotriphenylamine with 4-fuorobenzonitrile, followed by alkaline hydrolysis of the intermediate dinitrile compound **1**, according to the synthetic route outlined in Scheme 1. Elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the structures of the intermediate dinitrile compound **1** and the dicarboxylic acid monomer **2**. The transformation of cyano to carboxylic acid functionality could be monitored by the change of IR spectra (Figure 1). The cyano groups of compound **1** gave a characteristic band at 2219 cm^{-1} (stretching). After hydrolysis, the characteristic absorption of the cyano group disappeared, and the carboxylic acid group showed a typical carbonyl absorption band at 1674 cm^{-1} (C=O stretching) together with the appearance of broad bands around 2700–3400 cm^{-1} (O-H stretching). The structures of **1** and **2** were also confirmed by high-resolution NMR spectra. The ^{13}C NMR spectra of these compounds are given in Figure 2. The assignments of each carbon assisted by the 2-D NMR (Figures 3 and 4) also are given in the Figures, and these spectra are in good agreement with the proposed molecular structures. The ^{13}C NMR spectra confirm that the cyano groups were completely converted into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 120.43 ppm and the appearance of the carbonyl peak at 167.29 ppm. Other important evidence of this change is the shifting of the carbon resonance signals of C^{1} adjacent to the cyano or carboxyl group. The C^{1} of dinitrile **1** resonated at a higher field (99.01 ppm) than the other aromatic carbons because of the anisotropic shielding by the π electrons of C≡N. After hydrolysis, the resonance peak of C^{1} shifted to a lower field (128.10 ppm) because of the lack of an anisotropic field. The molecular structure of dicarboxylic acid compound **2** was also confirmed by X-ray crystal analysis acquired from the single crystal obtained by slow crystallization of an acetonitrile solution of **2**. As shown in Figure 5, compound **2** displays a propeller-shaped configuration of the triphenylamine cores, and the benzene rings are not in the same plane. This conformation will hinder the close packing of polymer chains and enhance the solubility of formed poly(amine-amide)s.

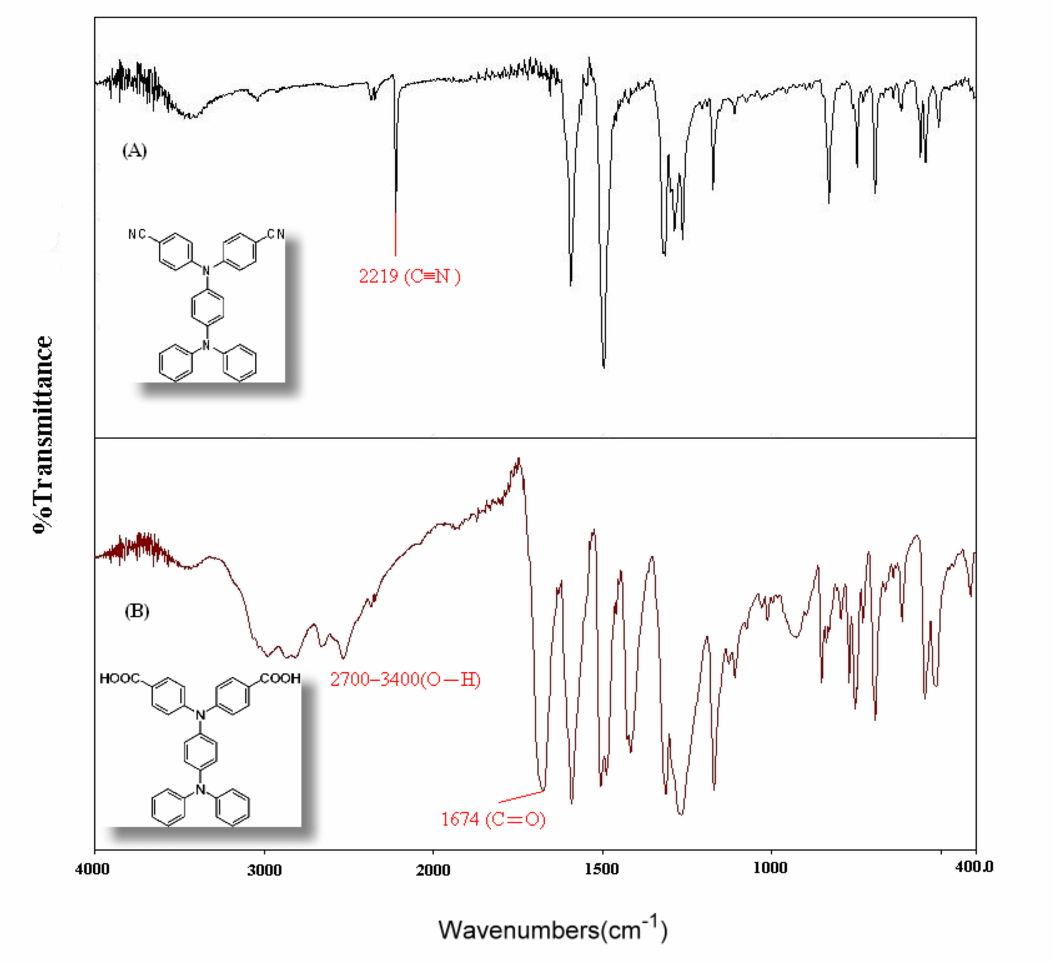


Figure S1. IR spectra of (A) dinitrile compound **1** (b) dicarboxylic acid compound **2**

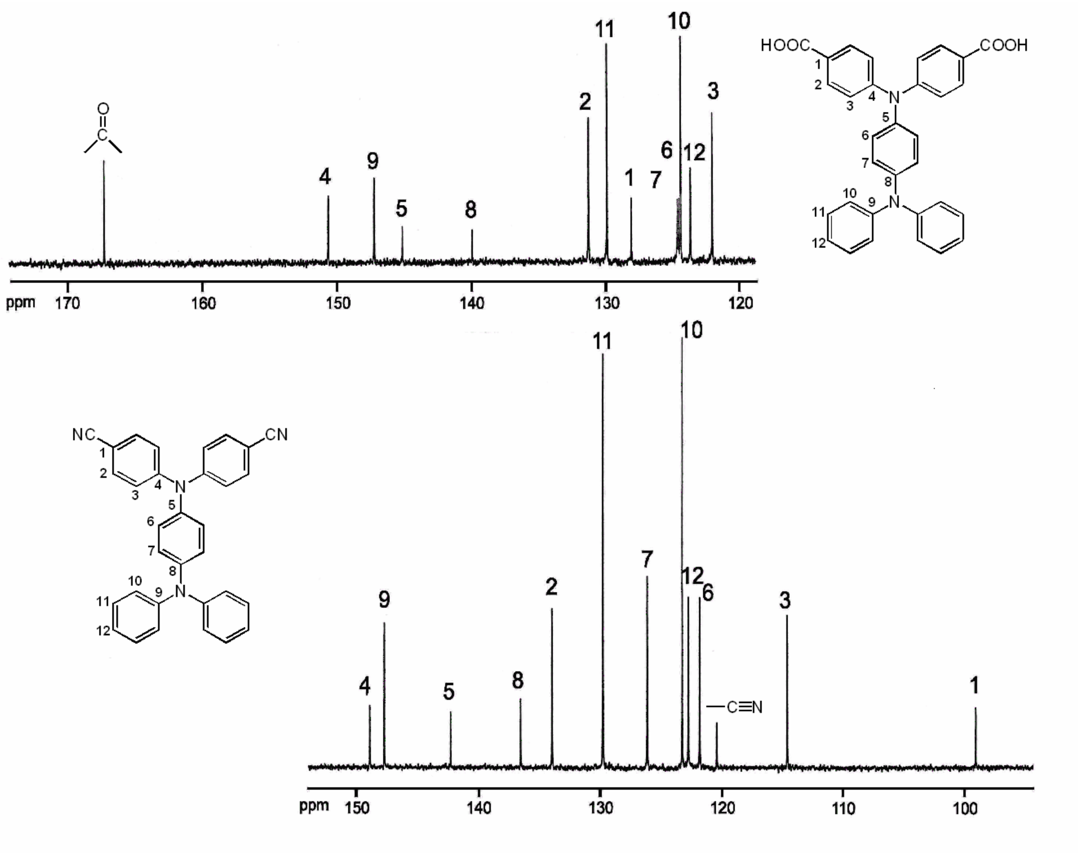


Figure S2. ^{13}C NMR spectra of dinitrile compound **1** and the dicarboxylic acid monomer **2** in DMSO-*d6*

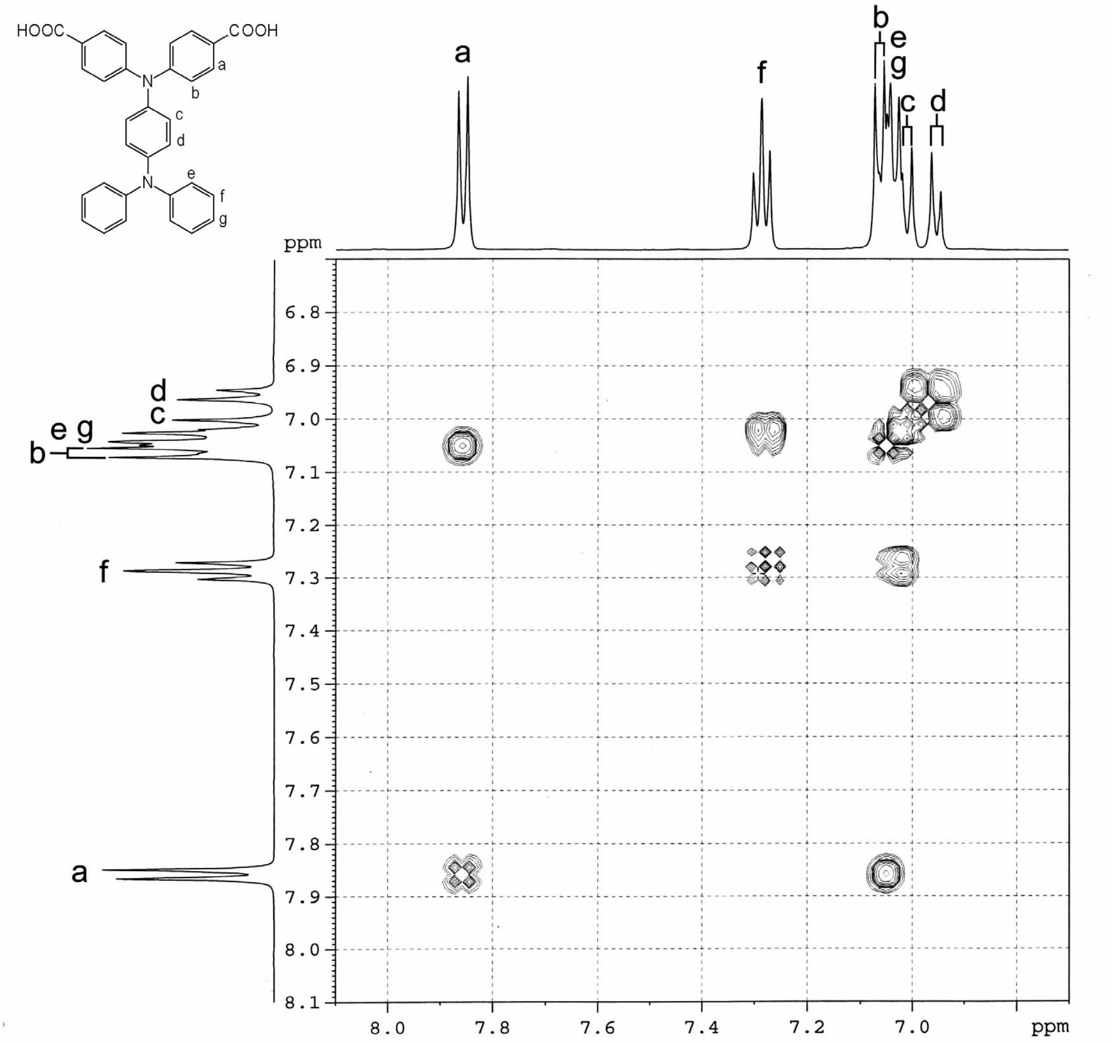


Figure S3. H–H COSY spectrum of compound **2** in DMSO-*d6*

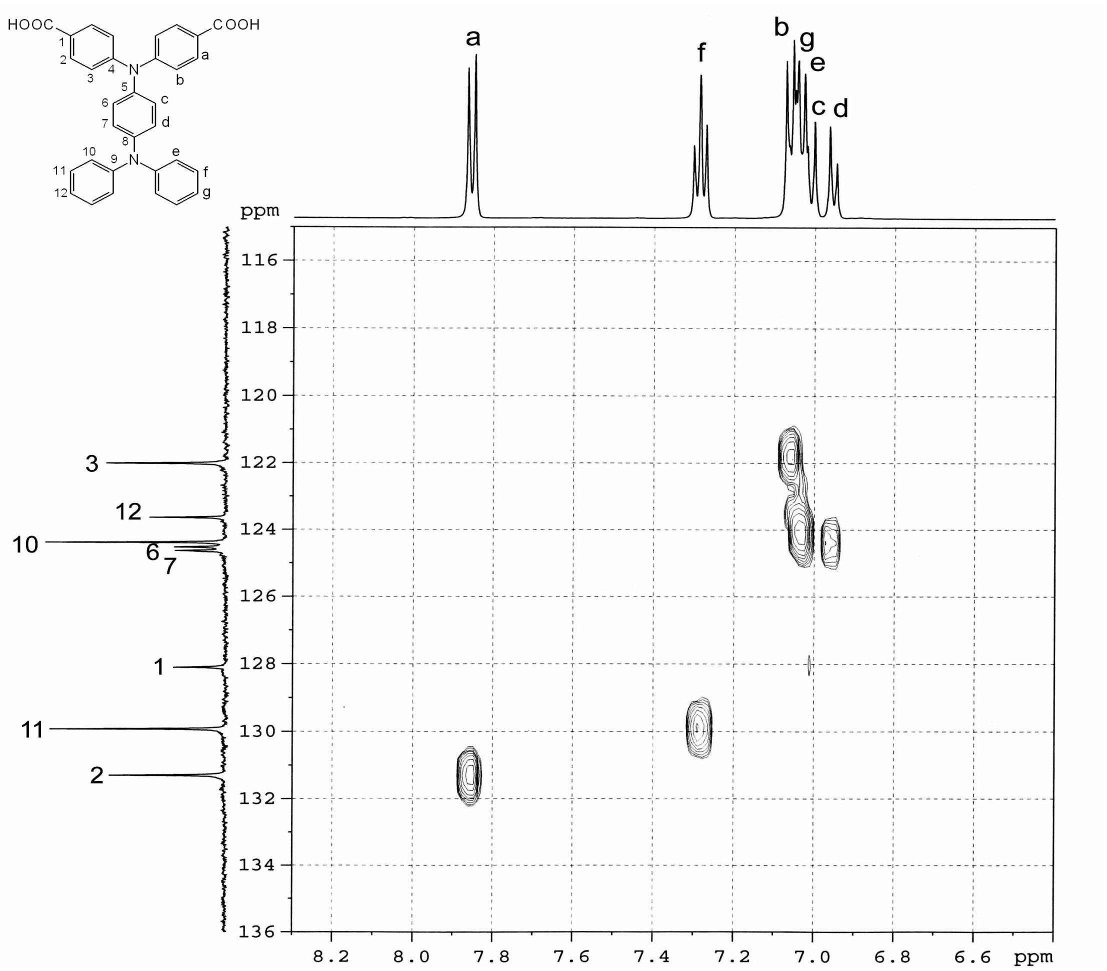


Figure S4. C–H COSY spectrum of compound **2** in DMSO-*d6*

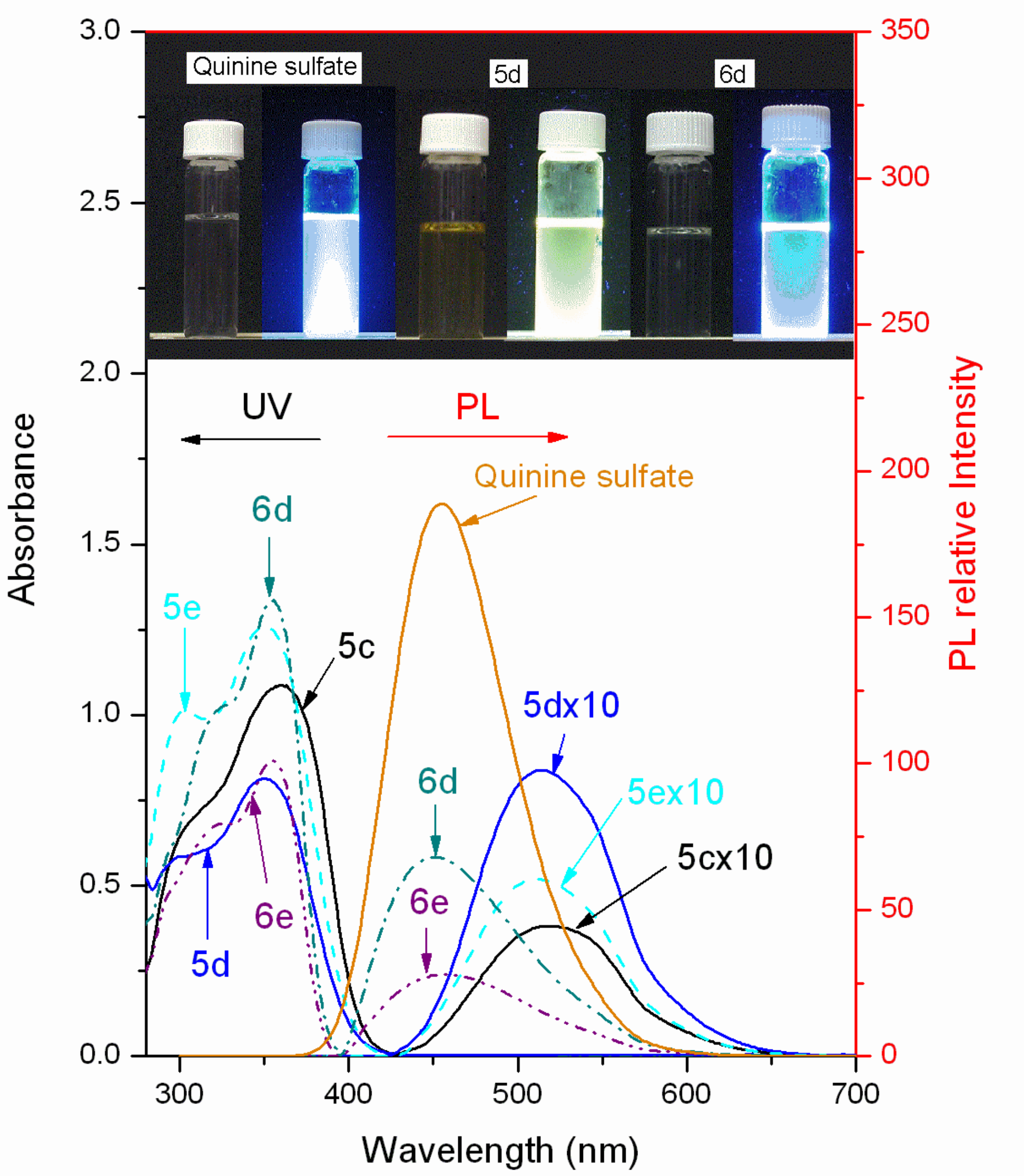


Figure 3 (Colour). Absorption and PL spectra of poly(amine-amide)s with a concentration of NMP (5 mg mL^{-1}). Quinine sulfate dissolved in 1 N H_2SO_4 (aq) with a concentration of (7.8 µm mL^{-1}), assuming ΦPL of 0.55.

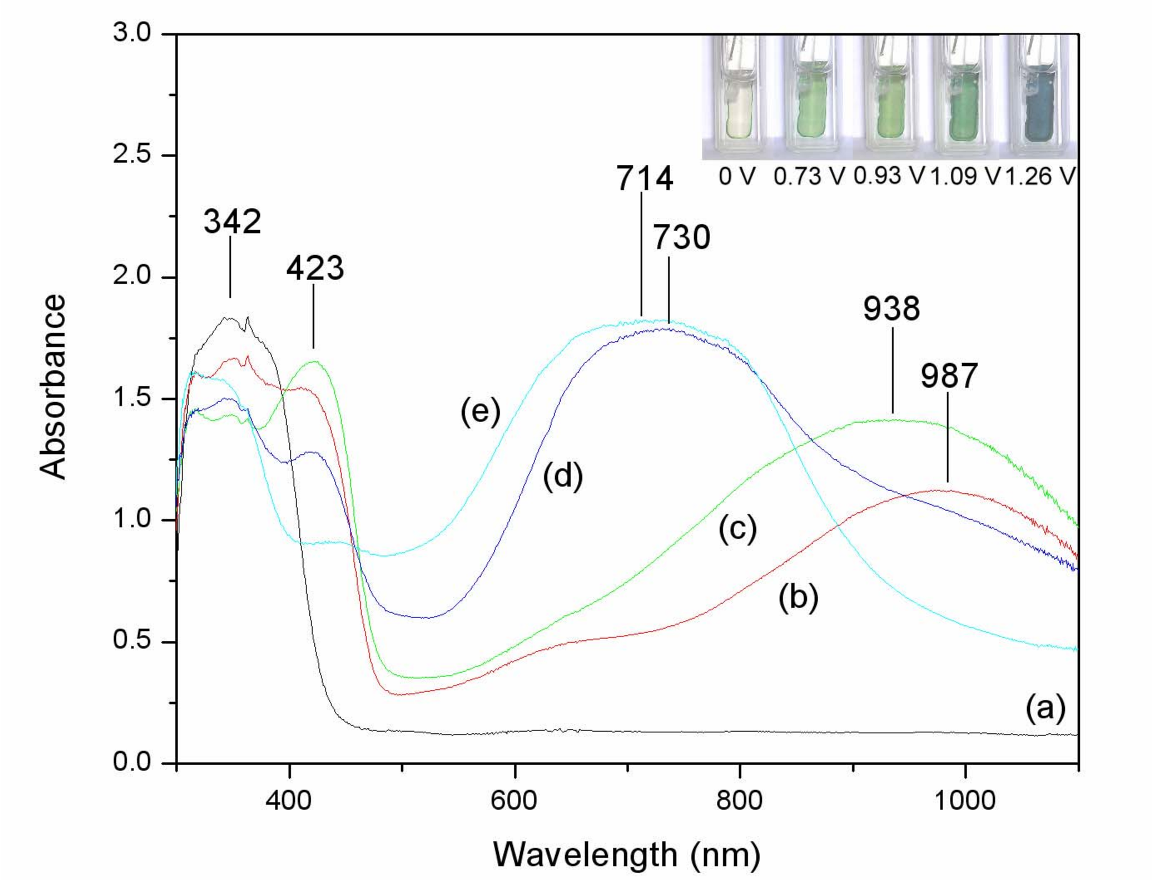


Figure 6 (Colour). Electrochromic behavior of poly(amine-amide) **5a** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte at (a) 0 (b) 0.73 (c) 0.93 (d) 1.09 (e) 1.26 V.

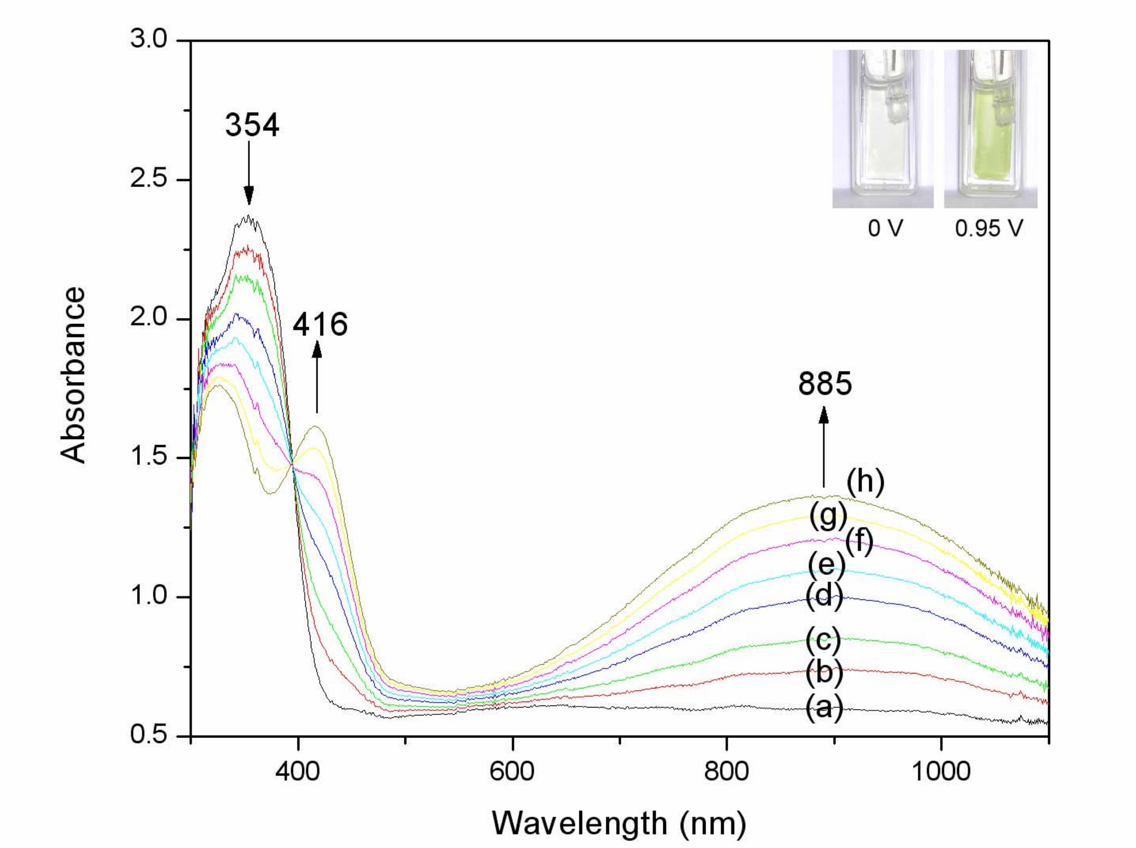


Figure 7 (Colour). Electrochromic behavior of poly(amine-amide) **5c** thin film (in CH3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0 (b) 0.70 (c) 0.73 (d) 0.77 (e) 0.80 (f) 0.83 (g) 0.85 (h) 0.95 V

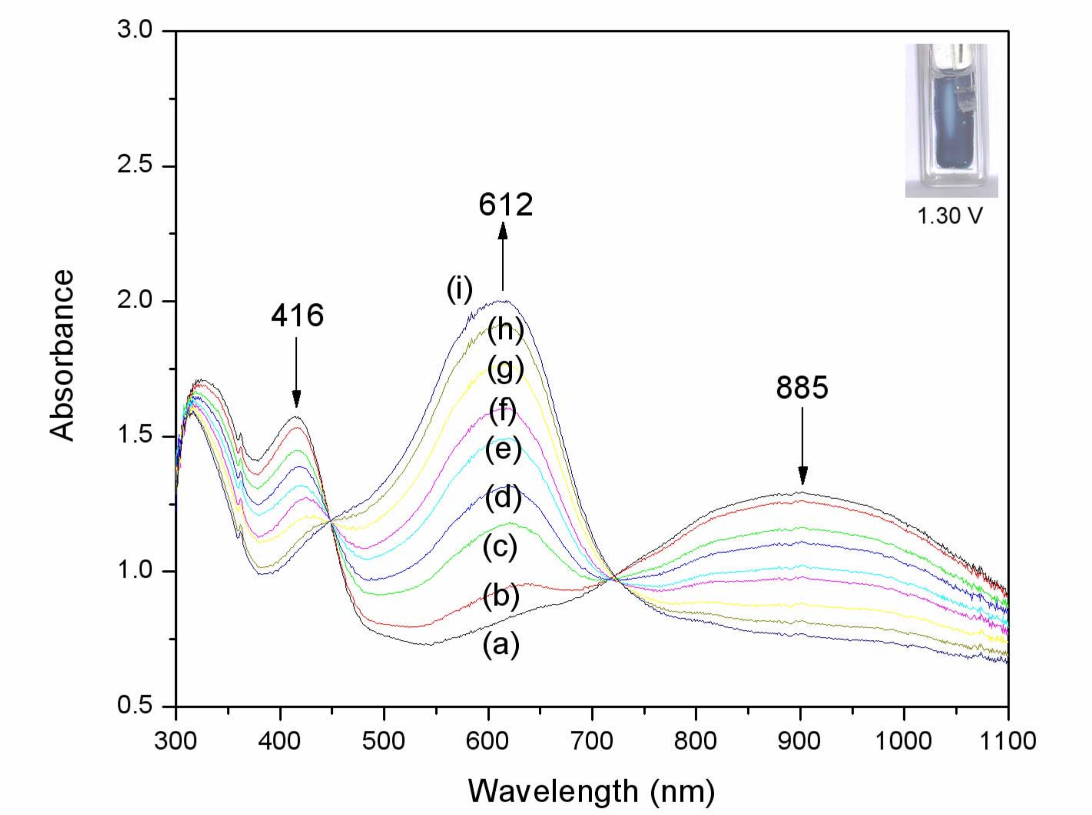


Figure 8 (Colour). Electrochromic behavior of poly(amine-amide) **5c** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolye) at (a) 1.01 (b) 1.05 (c) 1.07 (d) 1.10 (e) 1.13 (f) 1.16 (g) 1.19 (h) 1.25 (i) 1.30 V.