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New soluble triphenylamine-based amorphous aromatic polyamides for high performance blue-emitting hole-transporting and anodically electrochromic materials

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Abstract

A newly 4-methoxy-substituted triphenylamine-containing aromatic diacid monomer, 4,4′-dicarboxy-4″-methoxytriphenylamine **2**, with blue light (454 nm) fluorescence quantum efficiency 45% was successfully synthesized by the sodium hydride-mediated condensation of 4-methoxy-aniline with 4-fluorobenzonitrile, followed by alkaline hydrolysis of the intermediate dicyano compound. A series of novel aromatic polyamides having strong fluorescence emissions in the blue region with high quantum yields up to 40% and one reversible oxidation redox couples at 1.08 V *vs.* Ag/AgCl in acetonitrile solution have been synthesized and characterized. They exhibited good thermal stability with 10% weight-loss temperatures above 460 °C under a nitrogen atmosphere with relatively high glass-transition temperatures (267–307 °C). All obtained polyamides revealed excellent stability of electrochromic characteristics, changing color from original pale yellowish to blue.
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1. Introduction

Arylamine-containing aromatics have attracted considerable interest as hole-transport materials for use in multilayer organic electroluminescence (EL) devices due to their relatively high mobilities and their low ionization potentials [1–6]. The characteristic structural feature of triphenylamine (TPA) is the nitrogen center, the electroactive site of TPA, which is linked to three electron-rich phenyl groups in a propeller-like geometry. The anodic oxidation pathway of TPA was well reported [7] and the electrogenerated TPA cation radical dimerized to form tetraphenylbenzidine by loss of two protons per dimer, which is more easily oxidized than the TPA molecule. The electrochemical properties of TPA are affected when some of the hydrogen atoms are substituted with groups of different electronic strengths. In our previous studies it was found that TPA revealed lower oxidation potential and the formed cation radical was stabilized when electron-donating groups (methyl, methoxy) were substituted at the *para*-phenyl position [8–10]. The feasibility of utilizing spin-coating and ink-jet printing processes for large-area EL devices and possibilities of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive [11–19]. To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives involving hole-transporting units such as triarylamine, carbazole, and phenoxazine group in the emissive π-conjugated core/main chains [20–25] or grafting them as side chains in a polymer [26–29] or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges [30,31]. However, the solubility of many highly conjugated polymers is low, particularly for blue-emitting species. These

targeted blue-emitting polymers therefore often bear large alkyl, alkoxy, or aryloxy groups to improve solubility, thus lower their glass-transition temperatures (T_gs) and thermal stability.

To obtain high T_g hole-transporting polymers, many investigators have prepared polymers containing triphenylamine units in the main chain. Ogino et al. have successfully prepared triphenylamine-containing polymers which had hole-transporting ability [32,33]. Kakimoto et al. [34–36] reported that the charge injection and electroluminescent efficiency were improved remarkably by the incorporation of the hole-transporting polyimide containing triphenylamine moieties into the backbone. 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 [37–40], N,N-bis(4-carboxyphenyl)-N',N'-diphenyl-1,4-phenylenediamine [41], and 2,4-diaminotriphenylamine [42]. 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 [43,44]. In this article, we therefore design a novel class of *para*-methoxy-substituted triphenylamine-containing polyamides derived from the new dicarboxylic acid, 4,4'-dicarboxy-4''-methoxytriphenylamine **2** which is a blue light (454 nm) emitter with fluorescence quantum efficiency 45%, and various aromatic diamines. The general properties of these polymers 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.

2. Experimental

2.1. Materials

4-Methoxyaniline (Lancaster), sodium hydride (95%; dry ALDRICH), 4-fluorobenzonitrile (TCI), potassium hydroxide (TEDIA), N,N-dimethylacetamide (DMAc) (TEDIA), N,N-dimethylformamide (DMF) (ACROS), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP) (TEDIA), pyridine (Py) (TEDIA), and triphenyl phosphite (TPP) (ACROS) were used without further purification. Commercially available aromatic diamines such as *p*-phenylenediamine (TCI), *m*-phenylenediamine (TCI), and 4,4-oxydianiline (TCI) were used as received. Anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 3 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.

2.2. Monomer synthesis

#### 2.2.1. 4,4'-Dicyano-4''-methoxytriphenylamine (1)

A mixture of 4.80 g (0.20 mol) of sodium hydride and 180 mL of DMF was stirred at room temperature. To the mixture, 9.84 g (0.08 mol) of 4-methoxyaniline and 19.38 g (0.16 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 150 °C for 15 h under nitrogen and then precipitated into 400 mL of cold water. The products were filtered and recrystallized from DMAc to give green solid 13.28 g (yield: 51%); (mp = 174–176 °C; lit. [45] 173–176 °C) by DSC at 10 °C/min. IR (KBr): 2221.8 cm^{-1} (C≡N). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 3.76 (S, 1H, OCH$_3$), 7.00 (d, 4H, H$_c$), 7.06 (d, 4H, H$_b$), 7.12 (d, 2H, H$_d$), 7.68 (d, 4H, H$_a$). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm): 104.2 (C^1), 116.0 (CN), 119.3 (C^3), 122.0 (C^6), 129.4 (C^7), 132.5 (C^2), 137.6 (C^8), 150.0 (C^5), 160.0 (C^4). Calcd for C$_{21}$H$_{15}$N$_3$O (325.36 g/mol): C, 77.52%; H, 4.65%; N, 12.91%. Found: C, 77.32%; H, 4.68%; N, 12.87%.
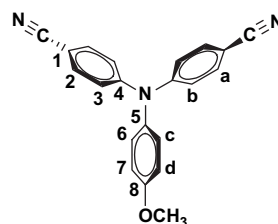
2.2.2. 4,4'-Dicarboxy-4''-methoxytriphenylamine (2)

A mixture of 4.12 g of potassium hydroxide and 1.71 g of the obtained compound **1** in 15 mL of ethanol and 20 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 yellowish precipitate was collected by filtration, washed thoroughly with water. It was recrystallized from acetic acid and then dried at 180 °C under vacuum to give 1.22 g (yield, 64%) of the diacid (mp = 278–281 °C by DSC at 10 °C/min). IR (KBr): 1672.8 (C=O), 2700–3400 cm^{-1} (O–H). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 3.75 (S, 1H, OCH$_3$), 6.95–7.06 (m, 4H, H$_b$ + H$_c$), 7.10 (d, 4H, H$_d$), 7.80 (d, 2H, H$_a$), 12.50 (s, 1H, COOH). ^{13}C NMR (125 Hz, DMSO-d_6, δ, ppm): 54.8 (OCH$_3$), 116.0 (C^3), 120.9 (C^1), 124.2 (C^6), 129.0 (C^7), 130.5 (C^2), 138.1 (C^8), 150.4 (C^5), 157.9 (C^4), 167.6 (C=O). Calcd for C$_{21}$H$_{17}$NO$_5$ (363.36 g/mol): C, 69.41%; H, 4.72%; N, 3.85%. Found: C, 69.35%; H, 4.72%; N, 3.87%.
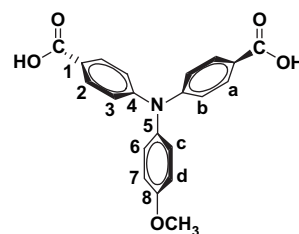
2.3. Polymer synthesis

The synthesis of polyamide **3c** is used as an example to illustrate the general synthetic route. The typical procedure is as follows. A mixture of 0.454 g (1.25 mmol) of the dicarboxylic
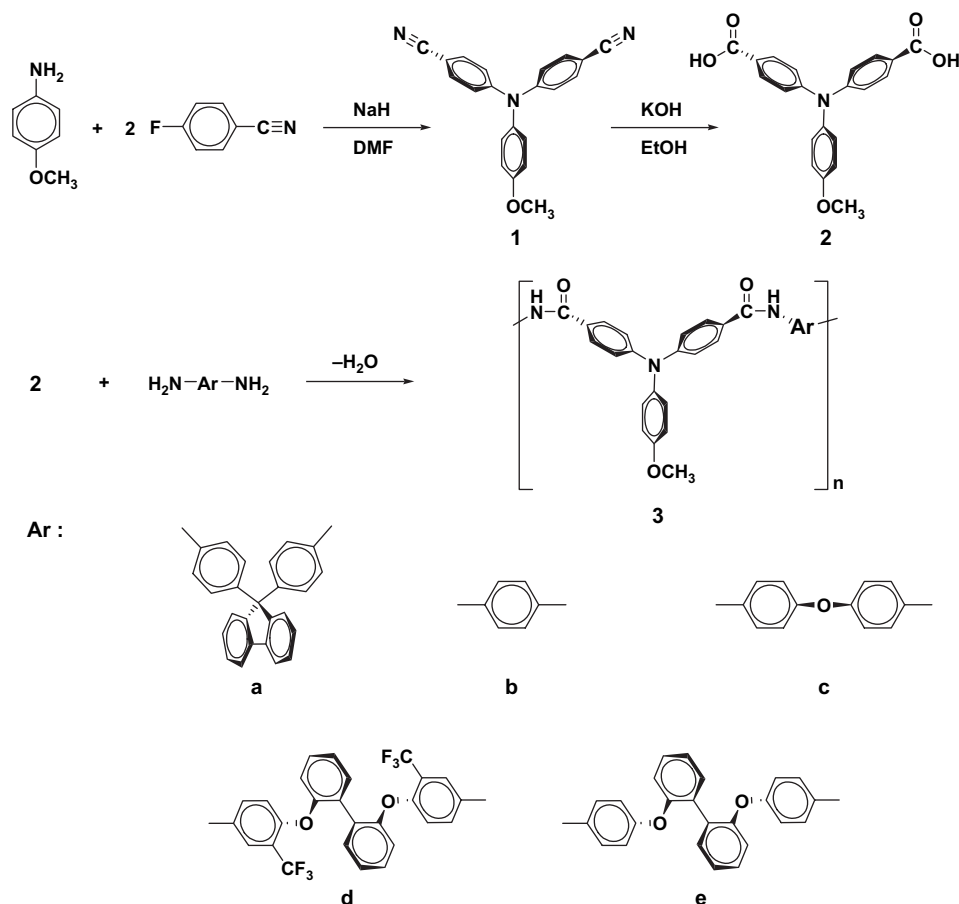
acid, 4,4′-dicarboxy-4″-methoxytriphenylamine **2**, 0.250 g (1.25 mmol) of 4,4-oxydianiline **c**, 0.15 g of calcium chloride, 0.9 mL of TPP, 0.6 mL of pyridine, and 2.5 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. The polymer that precipitated was collected by filtration, washed thoroughly with hot methanol, and dried at 150 °C for 15 h *in vacuo*. Precipitations from DMAc into methanol were carried out twice for further purification. The inherent viscosity of the obtained polyamide was 0.80 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. The IR spectrum of **3c** (film) exhibited characteristic amide absorption bands at 3299.1 (N–H stretching), 1646 cm^{-1} (amide carbonyl), 1245 cm^{-1} (C–O–C). Anal. Calcd for $(C_{33}H_{25}N_3O_4)_n$ (527.58 g/mol)$_n$: C, 75.13%; H, 4.78%; N, 7.96%. Found: C, 74.62%; H, 4.82%; N, 7.92%.

3. Results and discussion

3.1. Monomer synthesis

The new aromatic dicarboxylic acid having 4-methoxy-substituted triphenylamine unit, 4,4′-dicarboxy-4″-methoxytriphenylamine **2**, was synthesized by the amination reaction of 4-methoxyaniline with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dicyano compound, according to the synthetic routes outlined in Scheme 1. Elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the structures of the intermediate dicyano compounds **1** and the dicarboxylic acid monomer **2**. The IR spectra of compound **1** gave a cyano group characteristic band at 2222 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 1673 cm^{-1} (C=O stretching) together with the appearance of broad bands around 2700–3400 cm^{-1} (O–H stretching) (Fig. 1). The structures of compounds **1** and **2** were also confirmed by high-resolution NMR spectra (Figs. 2 and 3). 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 116 ppm and by the appearance of the carbonyl peak at 168 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 (104.2 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 (120.9 ppm) because of the lack of an anisotropic field.

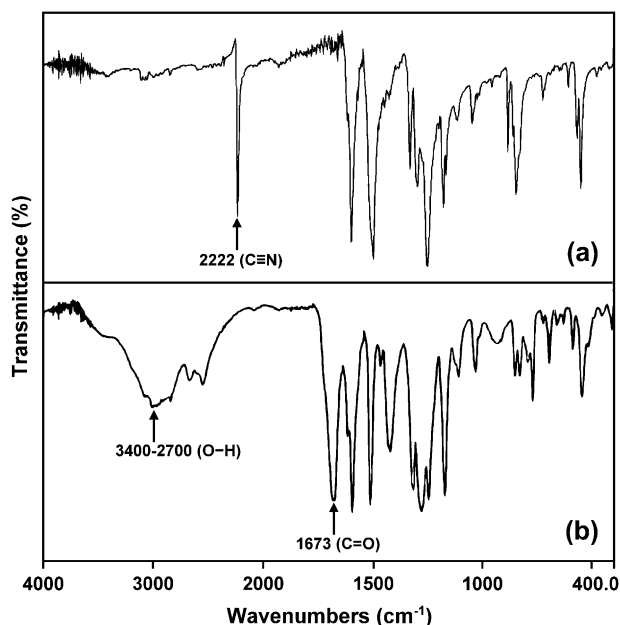Scheme 1. Synthesis of aromatic polyamides.

Fig. 1. The IR spectra of (a) dicyano compound **1** and (b) dicarboxylic acid compound **2**.

3.2. Polymer synthesis

A series of new aromatic polyamides with 4-methoxy-substituted triphenylamine units were prepared from the dicarboxylic acid **2** and various aromatic diamines by the direct polycondensation reaction with TPP and pyridine as condensing agents (Scheme 1). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions which when slowly poured into methanol precipitated in a fiber-like form. These polyamides were obtained in almost quantitative yields with inherent viscosity values in the range of 0.35–0.80 dL/g (Table 1) and the formation of polyamides was confirmed by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopies. Fig. 4 shows the IR spectra for polyamide **3c** with the characteristic absorption bands of the amide group around 3299 (N–H stretching), 1646 cm^{-1} (amide carbonyl). Fig. 5 summarizes a typical set of ^{1}H and ^{13}C NMR spectra of polyamide **3c** in DMSO-d_6, where all the peaks have been readily assigned to the hydrogen and carbon atoms of the recurring unit.
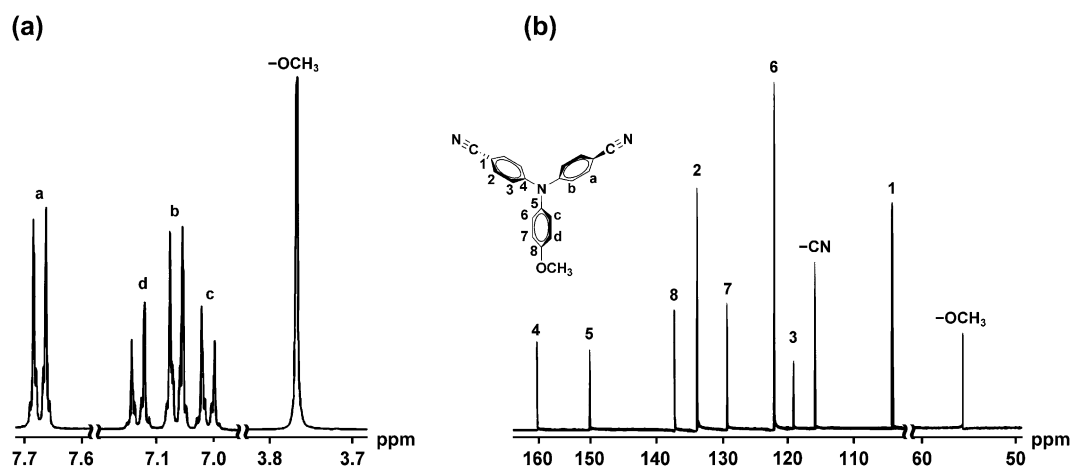

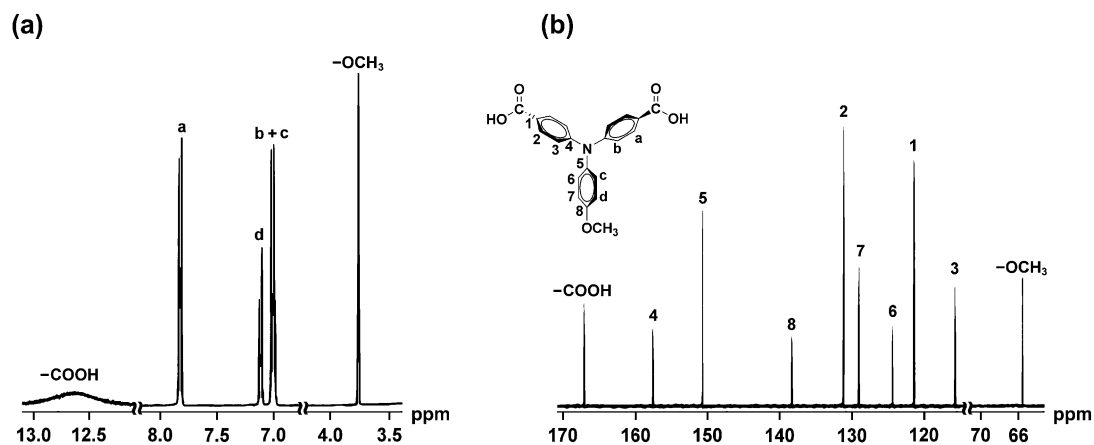Fig. 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound **1** in DMSO-d_6.

Fig. 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound **2** in DMSO-d_6.

Table 1
Solubility of aromatic polyamides

Polymer	η_{inh}^{b} (dL/g)	Solvents[a]						
		NMP	DMAc	DMF	DMSO	m-Cresol	THF	CHCl₃
3a	0.40	+	+	+	+	−	−	−
3b	0.48	+	+	+	+	+	−	−
3c	0.80	+	+	+	+	+	+	−
3d	0.35	+	+	+	+	+	+	−
3e	0.38	+	+	+	+	+	−	−

[a] Solubility: +, soluble at room temperature; −, insoluble even on heating.
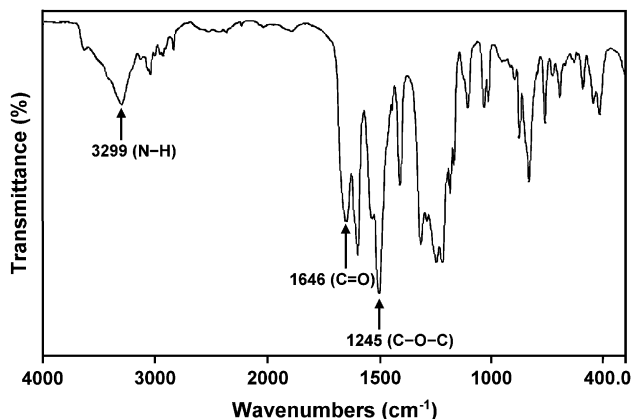[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

Fig. 4. The film FTIR spectra of polyamide **3c**.

3.3. Polymer properties

3.3.1. Basic characterization

The morphology of these polyamide films was characterized by wide-angle X-ray diffraction (WAXD) studies, and all the polyamides revealed amorphous patterns. The solubility behavior of these polyamides is also affected by the amorphous structure. All the polyamides were highly soluble in various polar solvents and the results are summarized in Table 1, and the enhanced solubility can be attributed to the presence of introduced triphenylamine units and the bulky pendent methoxy groups, which resulted in poor chain packing and decreased interchain interactions. Thus, the excellent

solubility makes these polymers as potential candidates for practical applications by spin- or dip-coating processes. All the aromatic polyamides could afford transparent and flexible films. The thermal properties of the polyamides were investigated by TGA and DSC. All the polyamides exhibited good thermal stability with insignificant weight loss up to 380 °C in nitrogen. The 10% weight-loss temperatures of the polyamides in nitrogen and air were recorded in the range of 460–500 and 455–485 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 51% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The T_gs of all the polymers could be easily measured by the DSC thermograms; they were observed in the range of 267–307 °C. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC scans.

3.3.2. Optical and electrochemical properties

The electrochemical and optical properties of the polyamides were investigated by cyclic voltammetry, UV–vis and photoluminescence spectroscopy. The results are summarized in Table 2. The UV–vis transmittance spectra of these polyamide films and the cutoff wavelengths (absorption edge, λ_0) in the range of 411–426 nm from the UV–vis spectra are also indicated in Fig. 6. These polymers exhibited strong UV–vis absorption bands at 360–370 nm in NMP solution, assignable to the π–π* transition resulting from the conjugation between the aromatic rings and nitrogen atoms. Their photoluminescence spectra in NMP solution and polymer thin film showed maximum bands around 465 nm in the blue region (Fig. 7). The strong fluorescence emissions in the blue region with high quantum yields up to 40% can be explained from the decreased intra- and intermolecular electronic interactions. The bulky, crank, and electron-withdrawing CF₃ group in diamines **a**, **e**, and **d**, respectively, were effectively in decreasing charge transfer formation within or between polymer chains through steric hindrance and inductive effect (by decreasing the electron-donating character of diamine moieties). The electrochemical redox behavior was investigated by cyclic voltammetry conducted for the cast film on an ITO-coated glass substrate as working
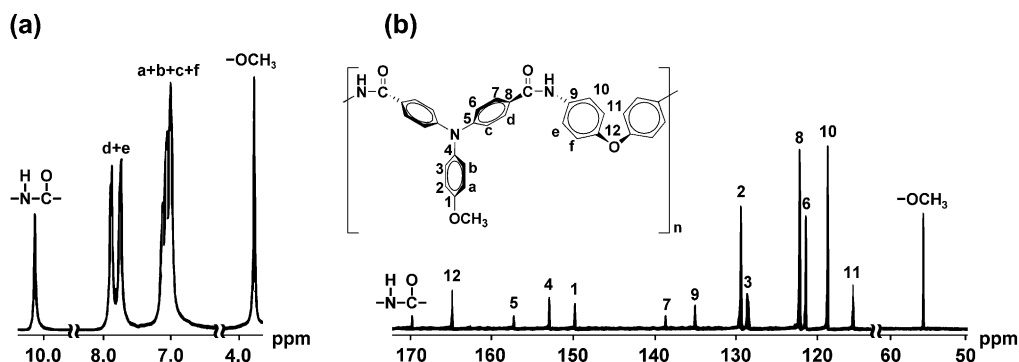

Fig. 5. (a) ¹H NMR and (b) ¹³C NMR spectra of polyamide **3c** in DMSO-d_6.

Table 2
Optical and electrochemical properties for the aromatic polyamides

Index	Color of film[c]	λ_0 (nm)[c]	$\lambda_{abs, max}$ (nm)[a]	$\lambda_{abs, onset}$ (nm)[a]	$\lambda_{PL, max}$ (nm)[b]	First oxidation (V) (vs. Ag/AgCl)	HOMO-LUMO Gap[d] (eV)	HOMO[e] (eV)	LUMO[f] (eV)	Φ_{PL}[g] (%)
3a	Pale yellowish	425	363(359)	398(406)	465(466)	1.08	3.05	5.44	2.39	40
3b	Pale yellowish	426	370(342)	403(421)	464(466)	1.00	2.95	5.36	2.41	8
3c	Pale yellowish	423	360(360)	400(423)	465(465)	1.02	2.93	5.38	2.45	25
3d	Off-white	418	363(361)	401(421)	465(466)	1.10	2.95	5.46	2.51	30
3e	Pale yellowish	411	360(360)	399(419)	465(461)	1.07	2.96	5.43	2.47	35

[a] UV–vis absorption measurements in NMP (1×10^{-5} M) at room temperature, values in parentheses are polymer thin films.
[b] PL spectra measurements in NMP (1×10^{-5} M) 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 (thickness: 50–70 μm).
[d] The data were calculated from thin film by the equation: gap = $1240/\lambda_{onset}$.
[e] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).
[f] LUMO = HOMO − gap.
[g] These values were measured by using quinine sulfate (dissolved in 1 N H_2SO_4 (aq) with a concentration of 10^{-5} M, assuming Φ_{PL} of 0.55) as a standard at 24–25 °C [46,47].
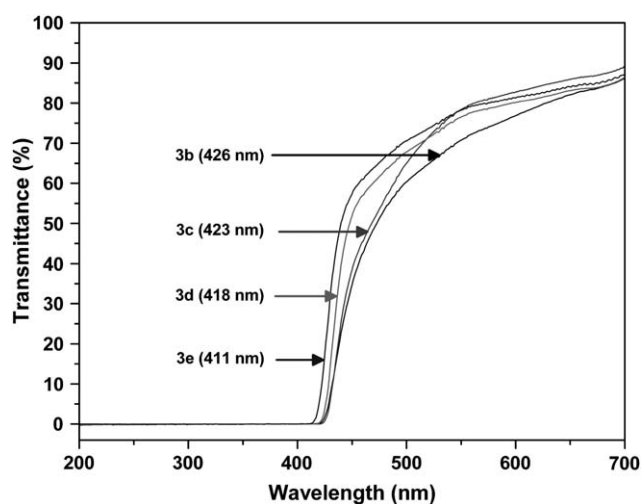

Fig. 6. Transmission UV–vis absorption spectra of some polyamides films.
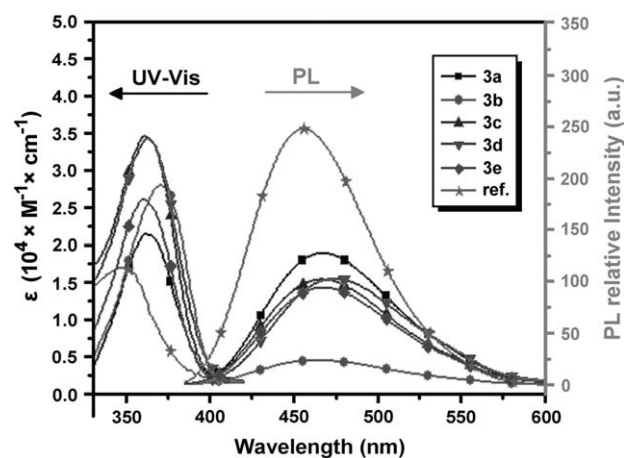

Fig. 7. Absorptions and PL spectra of polyamides 3a–3e with a concentration of NMP (1×10^{-5} M), quinine sulfate (ref.) dissolved in H_2SO_4 (aq) with a concentration of (1×10^{-5} M), assuming Φ_{PL} of 0.55.

electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for polyamide 3a are shown in Fig. 8 and showed one reversible oxidation redox couple at $E_{1/2} = 1.08$ V in the oxidative scan. Because of the electrochemical stability of the films and good adhesion between the polymer and ITO substrate, the polyamide 3a exhibited excellent reversibility of electrochromic characteristics by continuous five cyclic scans between 0.0 and 1.20 V, changing color from original pale yellowish to blue. The energy of the HOMO and LUMO levels of the obtained polyamides can be determined from the oxidation half-wave potentials and the onset absorption wavelengths and the results are listed in Table 2. For example, the oxidation half-wave potential for polyamide 3a has been determined as 1.08 V vs. Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard $E_{1/2}$ (Fc/Fc$^+$) is 0.44 V vs. Ag/AgCl in CH_3CN. Assuming that the HOMO level for the Fc/Fc$^+$ standard is 4.80 eV with respect to the zero vacuum level, the HOMO value for polyamide 3a could be evaluated to be 5.44 eV.
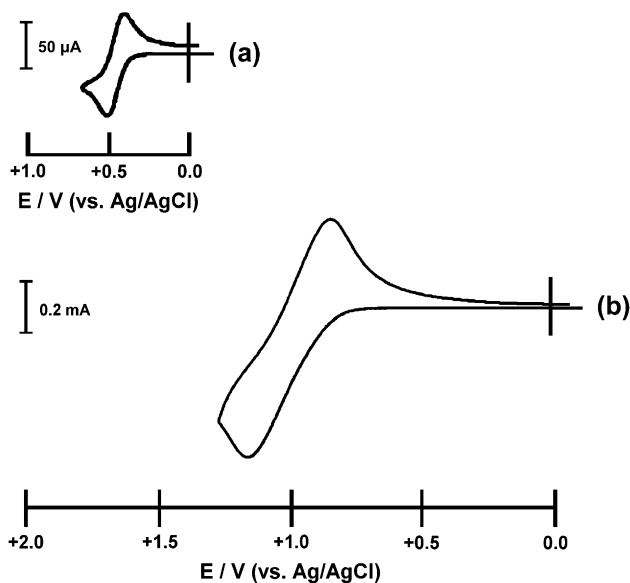

Fig. 8. Cyclic voltammograms of (a) ferrocene and (b) polyamide 3a film onto an indium-tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

3.3.3. Electrochromic characterization

The typical electrochromic absorption spectrum of polyamide **3a** is shown in Fig. 9. When the applied potentials increased positively from 0.0 to 1.20 V, the peak of characteristic absorbance at 362 nm, which is characteristic for polyamide **3a** decreased gradually while one new band grew up at 740 nm due to the first electron oxidation. The new spectrum was assigned as polyamide radical cation and the color of film **3a** changed from pale green to pale blue. The color switching times were estimated by applying a potential step, and the absorbance profiles are shown in Fig. 10. The switching time was defined as the time that is required to reach 90% of the full change in absorbance after applying potential. Thin film of polyamide **3a** would require 9 s at 1.20 V for switching absorbance at 740 nm and 8 s for bleaching. The polymer films still exhibited stability of electrochromic characteristic after five continuous scanning.
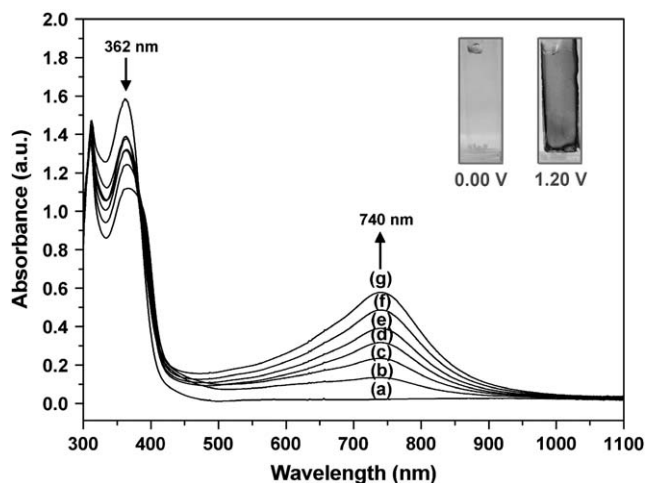

Fig. 9. Electrochromic behavior of polyamide **3a** thin film (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.95, (c) 1.00, (d) 1.05, (e) 1.10, (f) 1.15 and (g) 1.20 V.
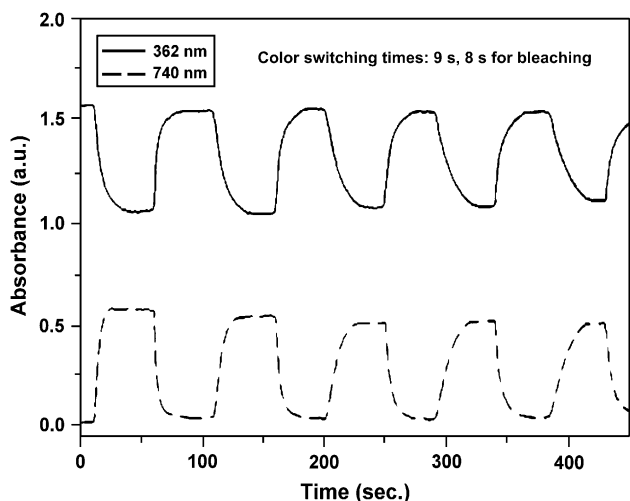

Fig. 10. Potential step absorptometry of polyamide **3a** (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0 V ⇆ 1.20 V).

4. Conclusions

A series of novel triphenylamine-based polyamides having strong fluorescence emissions in the blue region with high quantum yields up to 40% were successfully prepared from a new dicarboxylic acid, 4,4′-dicarboxy-4″-methoxytriphenylamine **2**, and various diamines. The results presented herein also demonstrated that incorporating bulky *para*-methoxy-substituted triphenylamine group into polymer backbone not only enhanced the processability of the rigid polymer backbone while maintaining good thermal stability but also revealed lower HOMO values, excellent electrochemical stability and electrochromic characteristics, changing color from the pale yellowish neutral form to the pale blue oxidized forms. Thus, these novel methoxy-substituted triphenylamine polyamides have a great potential as a new type of blue light-emitting hole-transporting and electrochromic materials due to their proper HOMO values, excellent electrochemical and thermal stabilities.

Acknowledgment

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