Pyrenylamine-Functionalized Aromatic Polyamides as Efficient Blue-Emitters and Multicolored Electrochromic Materials

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ABSTRACT: A series of novel aromatic polyamides with pyrenylamine in the backbone were prepared from a newly synthesized dicarboxylic acid monomer, *N*,*N*-di(4-carboxy-phenyl)-1-aminopyrene, and various aromatic diamines via the phosphorylation polyamidation technique. These polyamides were readily soluble in many organic solvents and could be solution-cast into tough and amorphous films. They had useful levels of thermal stability with glass-transition temperatures in the range of 276–342 °C and 10% weight loss temperatures in excess of 500 °C. The dilute *N*-methyl-2-pyrrolidone (NMP) solutions of these polymers exhibited fluorescence maxima around 455–540 nm with quantum yields up to 56.9%. The

INTRODUCTION Wholly aromatic polyamides (aramids) are considered to be high-performance polymeric materials because of their excellent thermal and oxidative stability, low flammability, and superior mechanical properties.¹ Highmodulus fibers of aramids were among the first highperformance polymers to be commercialized.² The most important products were Nomex[®] [poly(*m*-phenyleneisophthalamide)] and Kevlar[®] [poly(*p*-phenyleneterephthalamide)] fibers commercialized by DuPont in the late 1960s. The stiff polymer chains result not only in fibers with excellent mechanical properties but also in poor polymer solubility. The limited solubility is attributed to the very small entropy change during the dissolution process. The extremely high transition temperatures of the commercial aramids and their poor solubility in organic solvents lead to processing difficulties and limit their applications. As a result, research efforts have focused on enhancing their processability and solubility to expand the scope of the technological applications of these materials.³ In addition, there is currently a huge research effort directed toward exploiting the special functions of the polyamides by incorporating new chemical functionalities in the main chain or in the lateral structure.⁴

Pyrene is one of the most useful fluorogenic units for fluorescent sensors because it displays not only a well-defined monomer emission but also an efficient excimer emission.⁵ polyamides also showed remarkable solvatochromism of the emission spectra. Their films showed reversible electrochemical oxidation and reduction accompanied by strong color changes from colorless neutral state to purple oxidized state and to yellow reduced state. The polyamide **4g** containing the pyrenylamine units in both diacid and diamine sides exhibited easily accessible p- and n-doped states, together with multicolored electrochromic behaviors. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3475–3490, 2011

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In close enough proximity, an excited-state pyrene monomer and ground-state monomer can form an excimer state that fluoresces at a substantially longer wavelength than the monomer emission. It has also been shown that the intensity of the excimer emission can be enhanced by both inter- and intramolecular aggregation of pyrene monomers due to a greater probability of dimerization. The long fluorescence lifetime, large Stokes shift, and tunable intensity of the excimer make the pyrene unit a useful fluorophore labeling in metal ion or nucleic acid probes.⁶ In recent years, pyrene derivatives,⁷ polymers,⁸ starbursts,⁹ and dendrimers¹⁰ have been reported in the context of organic electronic applications such as organic light-emitting devices (OLEDs), because of their emissive properties combined with high charge carrier mobility. Although pyrene is a blue-emitting chromophore, the use of pyrene as emitting materials in OLED applications has been limited because of the aggregation between planar pyrene molecules. The high tendency toward π -stacking of the pyrene moieties generally lends the pyrenecontaining emitters strong intermolecular interactions in the solid state, which leads to a substantial red shift of their fluorescence emission and a decrease of the fluorescence quantum yields. Nonetheless, through molecular structure design, the close packing/fluorescence quenching effect in pyrenetype materials can be reduced or controlled. For example, a successful effort in the prevention of π -stacking in small

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molecules was achieved with 1,3,6,8-tetrasubstituted highly sterically hindered pyrenes,¹¹ which can emit blue light in solution as well as in the solid state with a high efficient yield. Additionally, diarylamino functionalized pyrene derivatives have been found to efficiently perform as emitters and charge transport materials in OLEDs.¹²

On the other hand, triarylamines are an important class of aromatic compounds because they could form stable aminium radical cations. Triarylamines can be building blocks for high spin polyradicals that showed ferromagnetic coupling.¹³ Perhaps most commonly, triarylamines have been used as the hole-transport layer in electroluminescent devices, 14,15 since the two-layered organic electroluminescent device using a bis(triphenylamine) as a hole-transfer layer was first reported by Tang and VanSlyke in 1987.¹⁶ Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylamine-based polymers have been developed for potential electrochromic applications.¹⁷ In recent years, Liou and coworkers have developed several high-performance polymers such as polyimides¹⁸ and polyamides¹⁹ carrying the triarylamine unit as a redox-chromophore. The triarylamine-containing monomers such as diamines and dicarboxylic acids could be easily prepared using well-established procedures,^{20,21} and they could react with the corresponding comonomers through conventional polycondensation techniques, producing the desired triarylamine-containing high-performance polymers. The polymers have high glass-transition and decomposition temperature. Because of the incorporation of packing-disruptive, propellershaped triarylamine units along the polymer backbone, the resulting polyamides generally exhibit good solubility in many organic solvents. They could afford tough and flexible films with good mechanical properties via simple solution processing, which is advantageous for their ready fabrication of large-area, thin-film devices. Thus, incorporation of threedimensional, packing-disruptive triarylamine units into the polyamide backbone not only resulted in enhanced solubility but also led to new electronic functions of polyamides, such as electrochromic characteristics. The electrochromic function of these polymers originates from the electroactive triarylamine moieties, which can be reversibly oxidized as long as the active sites of the aryl rings are protected. In addition, these electrochromic polyamides are transparent at the neutral state and can change to highly colorized at the oxidized states. This electrochromic behavior is different from that of the conjugated polymers extensively studied in recent years.²² Most of the reported conjugated polymers to be used as candidates for electrochromic applications are transparent at their oxidized state. To get the electrochromic device transmissive, it must be continuously kept under potential which may deteriorate the used polymers for fabrication in the time. As our reported triarylamine-based polyamides are highly transmissive at neutral state, it is safe to be used for this application and away from such possible deterioration.

In view of the attractive properties associated with the pyrene and triarylamine units, we have recently reported the synthesis of pyrenylamine-containing polyamides from N,Ndi(4-aminophenyl)-1-aminopyrene and aromatic or aliphatic dicarboxylic acids.²³ It was found that the polyamides display reversible oxidation and reduction processes, indicating their high electrochemical stability for both p- and n-doping of the diphenylpyrenylamine (DPPA) core. These polyamides also showed interesting fluorescent and electrochromic characteristics. However, the emission color of the reported pyrenylamine-based polyamides red shifted to yellowish green, and the quantum yield was not very high. This may be attributable to a lower energy gap of the chromophoric system. The reduced fluorescence quantum yield may also be explained by the quenching effect from the charge-transfer (CT) interactions between the pyrenylamine donor and the aroyl acceptor. The results are consistent with that reported by Kang and coworkers;²⁴ they studied the emission color tuning of 1,6-bis(N-phenyl-p-(R)-phenylamino)pyrenes and found that large red-shifted fluorescence emissions and lower quantum yields of the compounds are observed for R = -NPh₂ and -NMePh. They also demonstrated that the electron-withdrawing substituents, such as R = -CN and -F, led to deep blue emission and much higher quantum yields. In an attempt to obtain efficient blue-light-emitting pyrenylamine-based polymers, herein, we synthesize N,Ndi(4-carboxyphenyl)-1-aminopyrene as a new dicarboxylic acid monomer and its derived aromatic polyamides by direct polycondensation with various aromatic diamines. The resultant polyamides are expected to be good blue-emitters with an enhanced fluorescence efficiency as compared with their counterparts based on the previously reported N,N-di(4-aminophenyl)-1-aminopyrene,²³ because of the decreased highest occupied molecular orbital (HOMO) level and accordingly the increased energy gap together with the reduced inter- and intramolecular CT interactions.

EXPERIMENTAL

Materials

The starting material of 1-aminopyrene (mp: 115–116 °C) was synthesized by the electrophilic nitration of copper nitrate, followed by hydrazine Pd/C-catalytic reduction of intermediate nitro compound according to a previously reported procedure.²³ 4-Fluorobenzonitrile (TCI), cesium fluoride (CsF; Acros), and triphenyl phosphite (TPP; Acros) were used without further purification. N,N-Dimethylacetamide (DMAc; Tedia), N,N-dimethylformamide (DMF; Tedia), pyridine (Py; Tedia), and *N*-methyl-2-pyrrolidone (NMP; Tedia) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. p-Phenylenediamine (3a; TCI) and 9,9-bis(4-aminophenyl)fluorene (3e; TCI) were purified by sublimation in vacuo and recrystallization from ethanol, respectively. *m*-Phenylenediamine (**3b**; Acros), 4,4'-oxydianiline (3c; TCI), and 2,2-bis(4-aminophenyl)hexafluoropropane (3d: TCI) were used as received, 2',5'-Bis(4-amino-2-trifluoromethylphenoxy)-*p*-terphenyl (**3f**; mp: 222–223 $^{\circ}$ C)²⁵ and *N*,*N*di(4-aminophenyl)-1-aminopyrene (**3g**; mp: 227–229 °C)²³ were synthesized by the procedures reported previously.

Commercially obtained anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180 °C for 8 h before use. Tetrabutylammonium perchlorate (TBAClO₄; TCl) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* before use. Poly(methyl methacrylate) [PMMA; weight-average molecular weight (M_w) 120,000] and propylene carbonate (PC) were used as received from Aldrich and Acros Organic, respectively. All other reagents were used as received from commercial sources.

Synthesis of N,N-Di(4-cyanophenyl)-1-aminopyrene (1)

To a solution of 15.20 g (70 mmol) of 1-aminopyrene and 17.56 g (145 mmol) of 4-fluorobenzonitrile in 100 mL of dried dimethyl sulfoxide (DMSO), 22.79 g (150 mmol) of dried CsF was added with stirring all at once, and the mixture was heated at 170 °C for 18 h under nitrogen atmosphere. The mixture was poured into 1 L of water/methanol (1:1). The precipitated compound was collected by filtration and washed thoroughly by methanol and hot water. The crude product was filtered and recrystallized from acetic acid/water to afford 20.55 g (70% in yield) of pale brown needles with an mp of 241–242 °C (by differential scanning calorimetry (DSC) at a heating rate of 5 °C/min).

FTIR (KBr): 2218 cm⁻¹ (C=N stretch). ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 7.16 (d, J = 8.8 Hz, 4H, H_i), 7.70 (d, J = 8.8 Hz, 4H, H_k), 7.82 (d, J = 9.2 Hz, 1H, H_a), 7.98 (d, J = 8.2 Hz, 1H, H_d), 8.13 (t, J = 7.7 Hz, 1H, H_f), 8.18 (d, J = 9.3 Hz, 1H, H_b), 8.27 (d, J = 9.0 Hz, 1H, H_i), 8.30 (d, J = 9.0 Hz, 1H, H_h), 8.31 (d, J = 7.2 Hz, 1H, H_e), 8.39 (d, J = 7.6 Hz, 1H, H_g), 8.44 (d, J = 8.2 Hz, 1H, H_c). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 104.19 (C²⁰), 118.94 (C=N), 121.57 (C¹⁸ + C²), 123.72 (C⁴), 125.41 (C¹⁴), 125.84 (C⁸), 126.12 (C¹⁰), 126.71 (C⁵), 126.90 (C⁹), 127.13 (C¹³), 127.75 (C¹⁵), 127.90 (C⁶), 128.08 (C¹²), 129.22 (C³), 130.28 (C¹⁶), 130.54 (C¹¹), 130.57 (C⁷), 133.81 (C¹⁹), 137.19 (C¹), 150.13 (C¹⁷). Anal. Calcd (%) for C₃₀H₁₇N₃ (419.48): C, 85.90%; H, 4.08%; N, 10.02%. Found: C, 85.77%; H, 4.12%; N, 10.11%.



Synthesis of *N***,***N***-Di(4-carboxyphenyl)-1-aminopyrene (2)** A mixture of 5.35 g (95 mmol) of potassium hydroxide and 4.00 g (9.5 mmol) of the obtained dinitrile compound **1** in 30 mL of ethanol and 40 mL of distillated water was stirred at 110 °C until no further ammonia was generated. The time taken to reach this stage was about 4 days. The solution was

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filtered while hot and cooled to room temperature, and the pH value of filtrate was adjusted to near 3 by 3 M hydrochloric acid (HCl). The yellow precipitate was filtered, washed thoroughly with water, and recrystallized from acetic acid/water to afford 3.86 g (88.5% in yield) of pale yellow needles with a mp of 312–314 $^{\circ}$ C (by DSC at 5 $^{\circ}$ C/min).

FTIR (KBr): 2700–3200 cm⁻¹ (O—H stretch), 1682 cm⁻¹ (C=O stretch). ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 7.11 (d, J = 8.8 Hz, 4H, H_i), 7.86 (d, J = 8.8 Hz, 4H, H_k), 7.96 (d, J = 8.1 Hz, 1H, H_a), 7.99 (d, J = 9.3 Hz, 1H, H_d), 8.11 (t, J = 7.6 Hz, 1H, H_i), 8.15 (d, J = 9.3 Hz, 1H, H_c), 8.25 (d, J = 9.1 Hz, 1H, H_i), 8.27 (d, J = 9.1 Hz, 1H, H_h), 8.28 (d, J = 7.5 Hz, 1H, H_e), 8.37 (d, J = 7.6 Hz, 1H, H_g), 8.43 (d, J = 8.2 Hz, 1H, H_b). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 120.82 (C¹⁸), 121.96 (C⁶), 123.82 (C⁴), 124.20 (C²⁰), 125.47 (C¹⁴), 125.64 (C⁸), 125.91 (C¹⁰), 126.64 (C³), 126.80 (C⁹), 127.18 (C¹³), 127.74 (C¹²), 127.76 (C¹⁵), 127.92 (C²), 128.80 (C⁵), 130.13 (C¹⁶), 130.34 (C¹¹), 130.63 (C⁷), 131.06 (C¹⁹), 138.41 (C¹), 150.73 (C¹⁷), 166.79 (C=O). Anal. Calcd (%) for C₃₀H₁₉NO₄ (457.48): C, 78.76%; H, 4.19%; N, 3.06%. Found: C, 77.82%; H, 4.23%; N, 3.09%.



Synthesis of Polyamides

The synthesis of polyamide **4a** was used as an example to illustrate the general synthetic route. A mixture of 0.421 g (0.92 mmol) of diacid monomer **(2)**, 0.100 g (0.92 mmol) of *p*-phenylenediamine **(3a)**, 0.1 g of calcium chloride, 1.0 mL of TPP, 0.4 mL of pyridine, and 1.5 mL of NMP was heated with stirring at 120 °C for 3 h. The obtained polymer solution was poured slowly into 200 mL of stirred 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. Reprecipitations of the polymer by DMAc/methanol were carried out twice for further purification. The inherent viscosity of the obtained polyamide **4a** was 0.85 dL/g, measured at a concentration of 0.5 g/dL in 5 wt % LiCl DMAc at 30 °C.

FTIR (film): 3311 (amide N—H stretch), 1649 cm⁻¹ (amide C=O stretch). ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm): 7.13 (d, J = 8.2 Hz, 4H, H_i), 7.68 (s, 4H, H_i), 7.89 (d, J = 8.2 Hz, 4H, H_k), 7.96 (d, J = 7.9 Hz, 1H, H_a), 8.04 (d, J = 9.3 Hz, 1H, H_c), 8.12 (t, J = 8.2 Hz, 1H, H_f), 8.15 (d, J = 9.2 Hz, 1H, H_d), 8.25 (s, 2H, H_i + H_h), 8.27 (d, J = 7.7 Hz, 1H, H_e), 8.35 (d, J = 7.2 Hz, 1H, H_g), 8.42 (d, J = 7.7 Hz, 1H, H_b), 10.09 (s, 2H, amide N—H).



Preparation of the Polyamide Films

A solution of polymer was made by dissolving about 0.5 g of the aramid sample in 10 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven for 5 h to remove most of the solvent; then, the semidried film was further dried *in vacuo* at 180 °C for 8 h. The obtained films were about 70–90 μ m in thickness and were used for X-ray diffraction measurements, solubility tests, and thermal analyses.

Fabrication of Electrochromic Device

Electrochromic polymer films were prepared by dropping solutions of the aramids (4 mg/mL in DMAc) onto an indium tin oxide (ITO)-coated glass substrate ($20 \times 30 \times 0.7 \text{ mm}^3$, $50-100 \Omega$ /square). The polymers were drop-coated onto an active area of letters TTU using a mask. A gel electrolyte based on PMMA (M_w : 120,000) and LiClO₄ was plasticized with PC to form a highly transparent and conductive gel. The gel electrolyte was prepared as follows. PMMA (3 g) was dissolved in dry acetonitrile (15 g), and LiClO₄ (0.3 g) was added to the polymer solution as supporting electrolyte. Then, PC (5 g) was added as plasticizer. The mixture was then slowly heated until gelation. The gel electrolyte was spread on the polymer-coated

side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

Measurements

Infrared spectra were recorded on a Horiba FT-720 FT-IR spectrometer. Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE-500 FT-NMR using tetramethylsilane as the internal standard. The inherent viscosities were determined at 0.5 g/dL concentration using Cannon-Fenske viscometer at 30 °C. $M_{\rm w}$ and number-average molecular weights (M_n) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-Kα radiation. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on \sim 3–5 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm³/min). Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 to 350 °C at a scan rate of 10 °C/min 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. Absorption spectra were measured with an Agilent 8453 UV-visible diode array spectrophotometer. Fluorescence (FL) spectra were measured with a Varian Cary Eclipse fluorescence spectrophotometer. Fluorescent quantum yield was determined using solutions in NMP and was calculated



SCHEME 1 Synthetic route to the diacid monomer **2**.



FIGURE 1 (a) ¹H, (b) ¹³C, (c) H–H COSY, and (d) C–H HMQC NMR spectra of the target diacid monomer 2 in DMSO-d₆.



SCHEME 2 Synthesis of polyamides.

TABLE 1	Inherent Visco	sity and S	Solubility	Behavior	of
Polyamic	des				

Dalamaan	а	Solubility in Various Solvents ^b						
Code	η _{inh} (dL/g)	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	
4a	0.85	++	++	++	++	+	+-	
4b	0.49	++	++	++	++	+	+-	
4c	0.77	++	++	++	++	+	+-	
4d	0.38	++	++	++	++	++	++	
4e	0.50	++	++	++	++	+	+-	
4f	0.52	++	++	++	++	++	++	
4g	0.68	++	++	++	++	+	+-	
5a ^c	1.09	++	++	++	++	+	-	
5b	0.48	++	++	++	++	+	_	
5c	1.11	++	++	++	++	+	-	
5e	0.49	++	++	++	++	+	_	

 $^{\rm a}$ Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc–5 wt % LiCl at 30 $^{\circ}\text{C}.$

^b Solubility: ++, soluble at room temperature; +-, partially soluble; +, soluble on heating; and -, insoluble even on heating. Solvent: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; and THF, tetrahydrofuran.

 $^{\rm c}$ Structurally related polyamides with the corresponding Ar residue as in the 4 series analogs:



by comparing emission with that of a standard solution of 9,10-diphenylanthracene in cyclohexane (Φ_{FL} = 90%) at room temperature. Electrochemistry was performed with a CH Instruments 611C electrochemical analyzer. Cyclic voltammetry (CV) was conducted with the use of a threeelectrode cell in which ITO (polymer film area ca. 1 cm², 0.8 \times 1.25 cm²) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of at a home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.44 V vs. Ag/AgCl). Voltammograms are presented with the positive/negative potential pointing to the right/left with increasing anodic/decreasing cathodic current pointing upward/downward. Spectroelectrochemistry analyses were carried out with an electrolytic cell, which 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 in the spectroelectrochemical experiments were also measured with an Agilent 8453 UV-visible diode array spectrophotometer. A model HCPS-03-0310 laboratory Pulse Power Supply was used as the direct current power source to fix the potential between the two ITO electrodes of the device. Color measurements were performed by using Konica Minolta CS-100A ChromaMeter with viewing geometry as recommended by Commision Internationale de l'Eclairage.



FIGURE 2 TGA and DSC (inset) curves of polyamide **4g** with a heating rate of 20 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Monomer Synthesis

As shown in Scheme 1, the new pyrenylamine-based dicarboxylic acid monomer named as N,N-di(4-carboxyphenyl)-1-aminopyrene (2) was successfully synthesized by the CsF-assisted N,N-diarylation reaction of 1-aminopyrene with 4-fluorobenzonitrile in DMSO, followed by the alkaline hydrolysis of the intermediate dicyano compound 1 and the acidification of the resulting potassium carboxylate. Elemental and

TABLE 2 Thermal Properties of Polyamides^a

	T b	T 6	T _d at 1 Loss	7 _d at 10 wt % Loss ^d (°C)		
Index	7g [°] (°C)	/₅° (°C)	In N ₂	In Air	Yield° (%)	
4a	313	311	553	542	79	
4b	295	289	530	526	78	
4c	295	294	529	544	73	
4d	306	305	512	518	70	
4e	342	322	540	523	76	
4f	276	269	531	502	70	
4g	312	314	576	574	78	
5a	293	288	496	513	70	
5b	271	270	505	512	74	
5c	280	277	495	496	67	
5e	316	318	538	540	66	

 $^{\rm a}$ The polymer film samples were heated at 300 $^\circ {\rm C}$ for 1 h before all the thermal analyses.

^b The sample were heated from 50 to 400 °C at a scan rate of 20 °C/min followed by rapid cooling to 50 °C at –200 °C/min in nitrogen. The midpoint temperature of baseline shift on the subsequent DSC trace (from 50 to 400 °C at heating rate 20 °C/min) was defined as $T_{\rm g}$.

 $^{\rm c}$ Softening temperature measured by TMA using a penetration method. $^{\rm d}$ Decomposition temperature at which a 10% weight loss was recorded

by TGA at a heating rate of 20 °C/min.

 $^{\rm e}$ Residual weight percentages at 800 $^{\circ}{\rm C}$ under nitrogen flow.

TABLE 3 Absorption and Fluorescent Properties of Polyamides

	In So	As Solid Film (nm)					
Indexª	λ _{abs} (nm)	λ _{em} c (nm)	Φ_{FL} (%) ^d	λ _o	λ_{abs}	λ_{onset}	λ _{em} c
4a	362, 334 sh	458	33.0	426	363	431	465
4b	355, 334 sh	458	48.4	428	358	430	462
4c	353, 334 sh	458	52.3	430	355	435	464
4d	356, 334 sh	455	53.5	423	358	428	465
4e	353, 334 sh	458	56.4	426	355	433	463
4f	355, 331 sh	455	56.9	424	358	428	465
4g	370, 335	540	16.9	448	369	452	522
4′a	335, 385 sh	525	1.2	458	335	469	_e
4′b	335, 412 sh	533	25.0	457	336	465	509
4′c	335, 371 sh	536	26.1	456	336	467	509
4′d	335, 412 sh	531	8.8	455	334	461	513
5a	364	419	0.8	406	361	408	-
5b	355	421	7.7	404	361	405	453
5c	355	420	2.0	411	361	414	455
5e	355	422	10.4	408	360	412	452

 $^{\rm a}$ Analogous polyamides 4' having the corresponding isomeric repeat unit as those of the 4 series ones.

 $^{\rm b}$ The polymer concentration was 10 $^{-5}$ mol/L in NMP.

 $^{\rm c}$ Excited at the absorption maximum for both the solid and solution states.

 d The fluorescent quantum yield was calculated in an integrating sphere with 9,10-diphenylanthracene as the standard ($\Phi_{FL}=$ 90%).

^e Difficult to be defined because of low fluorescence intensity.



spectroscopic analyses were used to identify structures of the intermediate dicyano compound **1** and the target dicarboxylic acid monomer 2. The FTIR spectra of the synthesized compounds are illustrated in the Supporting Information Figure S1. The cyano groups of compound 1 gave characteristic bands at 2218 cm⁻¹. After hydrolysis, the characteristic absorptions of the cyano group disappeared, and the carboxylic acid group showed the typical C=O and O-H stretching absorptions at 1682 and 2700–3200 cm^{-1} , respectively. The NMR data of the intermediate dicyano compound 1 are included in the Supporting Information Figure S2. The ¹H, ¹³C, H—H COSY, and C—H HMQC NMR spectra of the target diacid monomer 2 are compiled in Figure 1. Assignments of each carbon and proton are also indicated in these spectra, and they are in good agreement with the proposed structures of these two compounds. The ¹³C NMR spectra confirm that the cyano groups were completely transformed into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 118.9 pm and the appearance of the carbonyl peak at 166.8 pm. Other important evidence of this transformation is the shifting of the carbon resonance

signals of C²⁰ adjacent to the cyano or carboxyl group. The C²⁰ of dicyano compound **1** resonated at a higher field (104.2 ppm) than the other aromatic carbons due to the anisotropic shielding by the cyano π -electrons. After hydrolysis, the resonance peak of C²⁰ shifted to a lower field (124.2 ppm) because of the lack of an anisotropic field. Thus, the spectroscopic data convincingly prove the successful synthesis of the target dicarboxylic acid monomer.

Polymer Synthesis

According to the phosphorylation polyamidation technique described by Yamazaki et al.,26 a series of novel aromatic polyamides 4a-4g with main-chain DPPA units were synthesized from the dicarboxylic acid monomer 2 with various aromatic diamines 3a-3g via solution polycondensation using TPP and pyridine as condensing agents (Scheme 2). Diamines 3a-e were obtained from commercial sources, whereas diamines 3f and 3g were synthesized according to the reported procedures.^{23,25} All the polymerization reactions proceeded homogeneously throughout the reaction and gave clear and highly viscous polymer solutions. The products precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured into stirring methanol. As shown in Table 1, the obtained polyamides had inherent viscosities in the range of 0.48-0.85 dL/g. The transparent and tough films can be obtained through solution-casting process which indicated the moderate to high molecular weight polyamides were achieved. For a comparative purpose, four structurally related polyamides 5a-c and 5e (see the footnote in Table 1) were also prepared from 4,4'-dicarboxytriphenylamine with the corresponding aromatic diamines in a similar synthetic procedure as that used for the 4 series polyamides. The molecular weight data of THF-soluble polyamides 4d and 4f were measured by GPC using polystyrenes as standard with THF as solvent. The M_w of polymers **4d** and **4f** were 32,500 and 45,000 with polydispersity index (M_w/M_n) of 2.03 and 1.88, respectively. The structures of the polyamides could be affirmed by IR and NMR spectroscopy. Supporting Information Figure S3 shows a typical IR spectrum for polyamide 4a. The characteristic IR absorption bands of the amide group appeared at around 3311 cm^{-1} (N–H stretch) and 1649 cm^{-1} (amide carbonyl). Supporting Information Figure S4 shows a typical set of ¹H and two-dimensional H-H COSY spectra of polyamide 4a in DMSO- d_6 . All the resonance peaks could be readily assigned to the hydrogen atoms in the repeating unit. The resonance signal appearing at 10.1 ppm in the ¹H NMR spectrum also supports the formation of amide linkages.

Solubility and Film Property

The solubility behaviors of polyamides **4a–4g** are also presented in Table 1. All the polymers were readily dissolved in highly polar organic solvents such as NMP, DMAc, DMF, and DMSO, attributed mainly to the introduction of bulky, three-dimensional DPPA unit into the polymer backbone. Polyamides **4d** and **4f** also showed good solubility in less polar solvents such as THF because of the additional contribution of the bulky trifluoromethyl ($-CF_3$) groups and



FIGURE 3 Normalized UV–vis absorption and fluorescence spectra of all polyamides with a concentration of 10^{-5} M in NMP. The fluorescence photographs of their NMP solutions and solid films (*ca.* 0.2 μ m) were taken under illumination of a 365 nm UV light.

laterally attached *p*-terphenyl segment. Thus, the excellent solubility makes these polymers potential candidates for practical applications by simple solution processing to afford high-performance thin films for optoelectronic devices. The

WAXD studies of these film samples indicated that all the polymers are essentially amorphous due to the presence of packing-disruptive DPPA units (see Supporting Information Figure S5).



FIGURE 4 UV–vis absorption and fluorescence spectra of aramids **4c** and **4'c** with a concentration of 10^{-5} M in NMP. The fluorescence photographs of their NMP solutions and solid films (*ca.* 0.2 μ m) were taken under illumination of a 365 nm UV light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties

The thermal stability and transition temperatures of the polyamides were investigated by TGA, DSC, and TMA techniques. A typical set of TGA and DSC curves of the representative polyamide 4g are shown in Figure 2, and the thermal data of all polyamides are summarized in Table 2. These polyamides show a high thermal stability; there is no obvious weight loss before the scanning temperature reaches 450 °C in nitrogen or in air. Their decomposition temperatures (T_d) at a 10% weight loss in nitrogen and air were recorded at 504-576 °C and 502-577 °C, respectively. The amount of carbonized residue (char yield) of these polymers was more than 68% at 800 °C in nitrogen atmosphere. The high char yields of these polymers can be ascribed to their high aromatic content. The glass-transition temperatures (T_{σ}) of the 4 series polyamides were observed in the range of 276–313 $^\circ C$ by DSC. The lowest T_g value (276 $^\circ C)$ of $\mathbf{4f}$ can be explained in terms of the decreased rotation barrier caused by the flexible ether linkages together with the increased free volume due to bulky pendent trifluoromethyl groups and the laterally attached *p*-terphenyl structure in the diamine component. As compared with the ${\bf 5}$ series analogs, the present series polyamides exhibit an increased $T_{\rm g}$ as a result of the presence of rigid pyrene units. The $T_{\rm s}$ (may be referred as apparent T_g) of the polymer films were determined by the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. The T_s values are also listed in Table 2. In most cases, the T_s values of these polyamides obtained by TMA are comparable to the T_g values measured by the DSC experiments. The thermal analysis results reveal that these polyamides exhibit high thermal stability, which in turn is beneficial to increase the operational lifetime in device application and enhance the morphological stability to the solution-processed films.

Absorption and Fluorescence Properties

The UV-vis absorption and fluorescence spectra of the polyamides were measured in dilute NMP solutions ($\sim 1 \times 10^{-5}$ mol/L) and as thin solid films, and the pertinent data are presented in Table 3. As shown in Figure 3, the absorption maxima of polyamides **4a**-**4f** lie in the range of 353-362 nm primarily because of the π - π * transition and n- π * transitions of the conjugated aromatic segments. Their emission maxima were at around 455-458 nm in the blue region with fluorescence quantum yields (Φ_{FL}) ranging from 33.0 to 56.9%. When compared with the corresponding **5** series counterparts, the higher quantum efficiency of the present series



FIGURE 5 Normalized UV–vis absorption and fluorescence spectra of the dilute solution of polyamide **4f** (*ca.* 10^{-5} M). Photographs were taken under illumination of a 365 nm UV light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyamides could be attributable to the presence of rigid, highly fluorescent pyrene chromophore. The spectral shifts in both absorption and fluorescence are very limited, indicating very small electronic perturbation of the Ar group in polyamides **4a–f**. In the solid state, **4a–f** showed similar absorption profiles as those measured in solution, with absorption maxima centered at 355–363 nm with absorption onset at 428–435 nm corresponding to optical bandgaps of 2.85–2.90 eV. As the photographs shown in Figure 3, **4a–f** in both solution and solid states showed strong blue fluorescence, suggesting that they are promising blue-emitting materials.

Different from **4a–f**, polyamide **4g** containing the pyrenylamine unit in both the diacid and diamine components showed a red-shifted absorption and emission together with a relatively lower quantum yield ($\Phi_{FL} = 16.9\%$). Yellowishgreen fluorescent polyamide **4g** had a lower quantum yield consistent with the energy gap law.²⁷ The fluorescent properties of polyamide **4g** is similar to those reported for the **4**' series analogs based on the previously reported *N,N*-di(4aminophenyl)-1-aminopyrene.²³ For comparison, the previously reported absorption and fluorescence data of four polyamides (**4**'**a**–**d**) with an isomeric repeating unit to that of the corresponding polyamides **4a–d** are also listed in Table 3. Obviously, all the 4 series polymers revealed a shorter wavelength emission and a higher fluorescence yield compared with the corresponding 4' counterparts. For a clearer comparison, the absorption and fluorescence spectra together with the fluorescence images of polyamides 4c and 4'c are illustrated in Figure 4. For the referenced polyamide 4'c, the absorption band at around 336 nm is attributed to $\pi - \pi^*$ and $n - \pi^*$ transitions of the conjugated aromatic segments, and that at longer wavelength (400-450 nm) may be assigned to inter- or intramolecular CT transitions from the DPPA donor to the benzoyl acceptor. The primary absorption band of polyamide **4c** shifted to a longer wavelength (\sim 355 nm) as compared with 4'c, which can be due to resonance interactions in the para amino-substituted benzoyl structure in the polymer backbone of 4c. The solution fluorescence peak wavelength (λ_{em}) of **4c** is located at 458 nm, and its full width at half maximum (FWHM) is 59 nm, which is about 40 nm smaller than $\mathbf{4'c}$ ($\lambda_{
m em}=$ 536 nm, FWHM =98 nm). Polyamide 4c is a blue light emitter in both solution and solid states, whereas 4'c is a yellowish-green or green light emitter. The quantum yield of $4^\prime c$ is much lower than that of 4c, possibly because of CT quenching. Thus, by changing the amide (-CONH-) orientation in these polyamide chains, it is possible to achieve the desired emission in the deep blue region of the visible spectrum with an enhanced quantum yield.

In contrast to absorption spectra, a strong medium effect is observed in the fluorescence spectra of these polyamides. For example, the absorption and PL spectra of the dilute solutions of polyamide **4f** in different solvents are illustrated in Figure 5. The emission maximum λ_{em} of **4f** in THF, NMP, and DMSO and its solid film appeared at 436, 455, 461, and 465 nm, respectively. The λ_{em} value increases as the solvent polarity increases. This clearly indicates that the polyamide stabilized in the excited state by the polar solvent molecules will display red-shifted emission. The large solvatochromism of the emission spectra also indicates that these polyamides permit strong intramolecular CT from the donor (pyrenyl-amine) to the acceptor (benzoyl).

Electrochemical Properties

The electrochemical behavior of these polyamides was investigated by CV conducted for the cast films on an ITO-coated glass substrates working electrode in dry acetonitrile (CH₃CN; for anodic oxidation) or DMF (for cathodic reduction) containing 0.1 M of TBAClO₄ as an electrolyte and saturated Ag/AgCl as reference electrode under nitrogen atmosphere. The derived oxidation and reduction potentials are summarized in Table 4. Figure 6(a) depicts the CV curve for polyamide 4c, which is representative for the other 4a-f analogs. Polymers 4a-f displayed a reversible reduction process at $E_{1/2}$ [$(E_{pa} + E_{pc})/2$] = -1.88 to -1.90 V and an irreversible oxidation process at $E_{\text{onset}} = 1.00-1.02$ V. The anodic wave originates from the oxidation of the DPPA segment, and the cathodic wave is attributable to the reduction of the pyrene group. The polyamide 4g exhibits the DPPA segment in both diacid and diamine components and displays an additional anodic oxidation wave at $E_{1/2} = 0.82$ V [Fig.

TABLE 4 Redox Potentials and Energy Levels of Polyamides

	Oxidation Potential (V) ^a	Reductio	Reduction Potential (V) ^b		FCV	FUOMORUMO
Index	<i>E</i> ^{ox} _{onset}	E ^{red} onset	$E_{1/2}^{\mathrm{red}}$	(eV) ^c	(eV) ^d	(eV) ^e
4a	1.00	-1.78	-1.90	2.88	2.78	5.36/2.58
4b	1.02	-1.77	-1.89	2.88	2.79	5.38/2.59
4c	1.01	-1.76	-1.88	2.85	2.77	5.37/2.60
4d	1.01	-1.78	-1.89	2.90	2.79	5.37/2.58
4e	1.02	-1.76	-1.88	2.86	2.78	5.38/2.60
4f	1.01	-1.74	-1.90	2.90	2.76	5.37/2.61
4g	0.71	-1.72	-1.90, -1.99 ^f	2.74	2.43	5.07/2.64
4′a	0.69	-1.82	-2.02	2.64	2.51	5.05/2.54
4′b	0.68	-1.80	-1.98	2.67	2.48	5.04/2.56
4′c	0.68	-1.84	-2.05	2.66	2.52	5.04/2.52
4′d	0.70	-1.77	-2.04	2.69	2.47	5.06/2.59
5a	1.02	-	-	3.04	-	5.38/2.34
5b	1.02	-	-	3.06	-	5.38/2.32
5c	1.03	-	-	3.00	-	5.39/2.39
5e	1.02	-	-	3.01	-	5.38/2.37

^a Versus Ag/AgCl in CH₃CN.

^b Versus Ag/AgCl in DMF. $E_{1/2}^{red}$: average potential of the redox couple peaks.

 c The data were calculated from polymer films by the equation: $E_g^{opt}=1240/\lambda_{onset}$ (optical energy gap between HOMO and LUMO).

^d Bandgap calculated from CV measurement.

^e The HOMO and LUMO energy levels were calculated from E_{onset}^{ox} and E_{onset}^{red} values of CV curves and were

referenced to ferrocene (4.8 eV relative to the vacuum energy level).

^f The values were determined by DPV measurements.

6(b)]. This oxidation process starting at about 0.71 V is reversible, indicating that the DPPA segment in the diamine residue could form a stable radical cation due to its more electron-rich nature. The second ($E_{pa} = 1.5$ V) oxidation peak is related the electron loss from the DPPA segment in the diacid component of polyamide 4g. Additionally, the cathodic reduction wave originating from the pyrene unit corresponds to a two-electron charging event because 4g contains the DPPA segment in both diacid and diamine residues. From the differential pulse voltammogram (DPV) of 4g shown in Figure 7(a) and the CV curves of the diamide model compounds M1 and M2 shown in Figure 7(b), we believe that the first reduction peak at $E_{\rm pc} = -1.85$ V appears to involve one electron charged into the pyrene unit of the diacid component, and the second reduction peak at $E_{\rm pc} = -1.96$ V arises from the second electron charged into the pyrene unit of the diamine component. However, these two reduction processes occurred almost simultaneously at the CV scan rate we used. Therefore, these two reduction waves merged and became indistinguishable in the CV diagram. Furthermore, a linear dependence of the peak currents as a function of scan rates confirmed both a nondiffusional redox process and a welladhered electroactive polymer film [Fig. 7(c,d)]. Because of the stability of the films and good adhesion between the polymer and ITO-glass substrate, 4g exhibited good redox stability during the first oxidation process.

On the basis of the oxidation and reduction onset potentials, the bandgaps for polyamides 4a-4f were calculated, and were found to vary from 2.76 to 2.79 eV. The bandgaps calculated from the CV measurements are somewhat lower (by 0.09-0.31 eV) than those obtained from the absorption spectra. By using the oxidation and reduction onset potentials, the HOMO levels for these polyamides were calculated and found to be 5.36-5.38 eV (relative to the vacuum energy level), whereas the values for the lowest unoccupied molecular orbital (LUMO) levels lay between 2.58 and 2.61 eV (Table 4), which are similar to those reported for the pyrene-containing triarylamines. As expected, the polyamide 4g possesses a higher HOMO energy (5.07 eV) and a smaller bandgap (2.43 eV) when compared with the 4a-f series. The relevant data for polyamide 4g are consistent with those reported previously for 4'a-d. This also suggests that attaching the carbonyl side of the amide linkage on the para positions of the DPPA phenyl units in the present polyamides results in a decrease in HOMO energy and an increase in bandgap.

Spectroelectrochemical and Electrochromic Properties

Spectroelectrochemical measurements were tested on films of polymers drop-coated onto ITO-coated glass slides immerged in electrolyte solution. The electrode preparations and solution condition were identical to those used in the CV experiments. The UV-vis–NIR absorption spectra of



FIGURE 6 Cyclic voltammograms of the cast films of polyamides (a) **4c** and (b) **4g** on an ITO-coated glass substrate in 0.1 M TBACIO₄ acetonitrile (for the anodic oxidation process) and DMF (for the cathodic reduction process) solutions at a scan rate of 50 and 100 mV/s, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyamide **4c** film at various applied potentials are shown in Figure 8, which is representative for the other 4a-4f counterparts. In the neutral form, polyamide 4c exhibited strong absorptions at 334 and 355 nm, characteristic for π - π * transitions, but it was almost transparent in the visible and NIR regions. The optical bandgap of polymer 4c was calculated as 2.85 eV from the onset of the π - π * transition at 435 nm. On electro-oxidation of the 4c film (increasing applied voltage from 0 to 1.45 V), the absorption of π - π * transition at 355 nm gradually decreased, whereas new peaks at 545 and 586 nm gradually increased in intensity. We attribute this spectral change to the formation of a monocation radical from the pyrenylamine moiety. The observed electronic absorption changes in the film of 4c at various potentials are associated with strong color changes; indeed, they even can be seen readily by the naked eye. From the photos shown in Figure 8(b) inset, it can be seen that the film changed from a nearly colorless transparent neutral state (L: 94.0; a: -4.0; and b: 18.0) to purple oxidized state (L: 65.5; a: 15.0; and b: -13.9). Dynamic changes in % transmittance of 355, 545, and 586 nm at varying applied potentials are illustrated in Figure 8(b). The electrochromic polymer 4c shows a relative high optical contrast in visible region with a transmittance change (% ΔT) of 44.7% at 545 nm and 46.8% at 586 nm

for purple coloring at electrode potential of 1.45 V. A similar spectral change was observed for analogous polyamides **4a**, **4b**, and **4d-f** during the oxidation process. For example, the spectroelectrochemical series of polyamide **4b** are included in the Supporting Information Figure S6. Moreover, color changes were also observed in these polyamides on reduction. Figure 8(a) inset illustrates the spectral and coloration changes of **4c** on electro-reduction. However, the color change (colorless to light yellow) is not strong as that observed in the anodic scanning.

The electro-optical properties of polyamide 4g were also deciphered using the changes in electronic absorption spectra on both oxidation and reduction process (Fig. 9). This polyamide exhibited ambipolar and multicolored electrochromic behaviors arising from the DPPA segments linked to different sides of the amide linkage. When the applied potentials increased positively from 0 to 1.0 and 1.5 V, corresponding to the first and second electron oxidation, the characteristic absorption bands at 335 and 369 nm for neutral-form polyamide 4g decreased gradually and bathochromically shifted to 549 and 594 nm, accompanied by the concomitant formation of new broad long-wavelength absorption bands centered on 834 nm. The spectral changes are apparently arisen from the sequential oxidation processes of the amino centers in the two DPPA segments of different electronic nature in the polymer backbone of 4g. As shown in Figure 9(a) inset, the polymer film showed a dualcolored electrochromic behavior on electro-oxidation, with a coloration change from pale yellow (L: 94.5; a: -6.7; and b: 50.0), through greenish-gray (L: 73.0; a: -9.0; and b: 23.2), and to dark purplish-gray (L: 46.0; a: 5.2; and b: -12.9). When the applied potentials increased negatively from 0 to -2.0 and -2.4 V, corresponding to the first and second electron reduction, the characteristic absorption bands at 335 and 368 nm for neutral-form polyamide 4g maintained their absorptions and accompanied by the concomitant formation of new sharp long-wavelength absorption bands centered on 503 nm in visible region. The spectral changes are apparently arisen from the sequential reduction processes of the pyrene units of slightly different electronic nature in the polymer backbone of 4g. As illustrated in Figure 9(b) inset, the polymer film of 4g changes from neutral pale yellow, through bright yellow (L: 85.0; a: 1.1; and b: 64.1) at -2.0 V, and to reddish-orange (L: 63.0; a: 52.1; b: 70.6) at -2.4 V. The possible oxidation and reduction orders of the redoxactive units of polyamide 4g are proposed in Figure 9(c). The $E_{\rm pa}$ and $E_{\rm pc}$ values indicated in each amino center and the pyrene units were taken from the CV or DPV diagram of 4g. Thus, the incorporation of DPPA units into both of the diacid and diamine components causes the polyamide to exhibit different oxidation states which make it to be a multicolored anodically and cathodically coloring material.

Electrochromic Stability

Electrochromic switching studies for the polyamides were performed to monitor the percent transmittance changes ($\Delta\%T$) as a function of time at their absorption maximum and to determine the response time by stepping potential



FIGURE 7 (a) DPV of the cast film of polyamide **4g** on the ITO-coated glass substrate in 0.1 M TBACIO₄/DMF solution for cathodic reduction process. Scan rate, 10 mV/s; pulse amplitude, 50 mV; pulse width, 50 ms; and pulse period, 0.2 s. (b) Cyclic voltammograms of 10 mM of diamide model compounds **M1** and **M2** in DMF containing 0.1 M TBACIO₄ at a Pt coil electrode, scan rate = 100 mV. (c) Cyclic voltammograms of polyamide **4g** films at various potential scan rates for the first anodic oxidation process. (d) Plots of the current densities versus the scan rates for polyamide **4g** films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 (a) Spectroelectrochemistry of the aramid **4c** thin film on the ITO-coated glass substrate in 0.1 M TBACIO₄/CH₃CN at various applied potentials. (b) Optical change in T% as a function of applied potential for the three absorption bands at 355, 545, and 586 nm. The photographs show the color change of the film on an ITO electrode at indicated potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 9 Spectral changes of the cast film of polyamide **4g** on the ITO-coated glass substrate on (a) p-doping 0.1 M TBACIO₄/ CH₃CN and (b) n-doping in 0.1 M TBACIO₄/DMF at various applied potentials (vs. Ag/AgCl). (c) The possible redox order for the DPPA segments in the repeating unit of polyamide **4g**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

repeatedly between the neutral and oxidized states. The active area of the polymer film on ITO-glass is $\sim 1 \text{ cm}^2$. As a typical example, Figure 10 depicts the optical transmittance and current density changes of polyamide **4g** as a function of time at their longer wavelength absorption maxima (597 and 834 nm) by applying squarewave potential steps of 11 s



FIGURE 10 Dynamic changes of (a) absorption, (b) current densities, and (c) optical transmittance monitored for polyamide **4g** at 834 nm, stepped between 0.0 and 1.00 V (vs. Ag/AgCl). The red solid-dot shows (d) the variation in the CE after different switching cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 11 (a) Photos of sandwich-type ITO-coated glass single layer electrochromic device, using polyamide **4g** as active layer. (b) Schematic illustration of the structure of the electrochromic device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.] (complete cycle time is 22 s) between 0 and 1.0 V. The response time was calculated at 90% of the full-transmittance change because it is difficult to perceive any further color change with naked eye beyond this point. Polyamide **4g** attained 90% of a complete coloring and bleaching switch in less than 4 s (3.8 s for coloring) and 2 s (1.6 s for bleaching), respectively. As shown in Figure 10(a,b), the absorbance changes at 834 nm reflect the switch in current, and the kinetics of the charge transport process can be referenced to the coloration response time. Coloration efficiency (CE; η) is a useful term for measuring the power efficiency of the electrochromic devices and can be calculated via optical density using the following equation:²⁸

$$\eta = \Delta OD(\lambda_{\rm max})/Q$$

where Q is the injected/extracted charge per unit electrode area (mC/cm²) and Δ OD is the change in absorbance at a specific wavelength maximum during a redox step. The CE for the **4g** film at 834 nm was calculated to be 112 cm²/C. The long-term stability of polyamides **4g** was investigated by monitoring the electrochromic contrast (Δ %*T*) of the thin films on repeated squarewave potential steps of 11 s in a 0.1 M Bu₄NClO₄/CH₃CN electrolyte solution between 0 and 1.0 V. In more than 100 cycles under ambient conditions, polyamide **4g** showed a variation of electrochromic contrast of less than 1%, whereas the CE exhibited decay of about 3.6% [Fig. 10(c,d)]. Therefore, the electrochromic switching behavior appears to be highly reversible during the first oxidation process of this polyamide.

Electrochromic Device

On the basis of the foregoing results, it can be concluded that these polyamides can be used in the construction of electrochromic devices and optical display due to the fast response time and the robustness of the polymers. Therefore, we fabricated as preliminary investigations single layer elecrochromic cells (Fig. 11). As a typical example, an electrochromic cell based on polyamide **4g** was fabricated. When the voltage applied was increased (to a maximum of 3.0 V), the color changed from pale yellow to light gray then to dark purplish-gray, similar to those observed for the solution spectroelectrochemistry experiments. We believe that optimization could further improve the device performance and fully explore the potential of these multicolored electrochromic polyamides.

CONCLUSIONS

A series of novel pyrenylamine-functionalized aromatic polyamides have been prepared from a newly synthesized diacid monomer, N,N-di(4-carboxyphenyl)-1-aminopyrene, with various aromatic diamines via the phosphorylation polyamidation reaction. All the polymers could form morphologically stable and uniform amorphous films using simple solutioncasting techniques. They also showed high T_g and good thermal stability. When comparing with the analogous polyamides based on N,N-di(4-aminophenyl)-1-aminopyrene, the present series polyamides displayed a blue-shifted emission in the deep blue region together with an enhanced fluorescence quantum efficiency. Reported properties prove that the polyamides are multifunctional materials which may find optoelectronic applications in OLEDs and electrochromic devices.

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