

Novel Aromatic Polyamides with Chromophoric *N,N*-Diphenyl-*N',N'*-di(4-*tert*-butylphenyl)-1,4-phenylenediamine Moieties: Synthesis, Luminescence, and Electrochromism

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Abstract

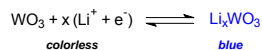
A new class of electroactive polyamides with di-*tert*-butyl-substituted *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine (TPPA) units were prepared via the direct phosphorylation polycondensation from a new dicarboxylic acid monomer, *N,N*-bis(4-carboxyphenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine (**2**), with various aromatic diamines. These polyamides were amorphous with good solubility in many organic solvents, such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc), and could be solution-cast into flexible polymer films. The polyamides exhibited good thermal stability with glass-transition temperatures in the range of 265–293 °C and 10% weight-loss temperatures in excess of 509 °C. The dilute solutions of these polyamides in NMP exhibited strong absorption bands centered at 351–361 nm and showed a green photoluminescence around 517–521 nm. Cyclic voltammograms of the polyamide films on the indium-tin oxide (ITO)-coated glass substrate in 0.1 M tetrabutylammonium perchlorate (TBAP) acetonitrile solution exhibited stable and well-defined reversible redox couples during oxidative scanning. The polyamide films also showed an interesting electrochromic property with the color change from a colorless or pale yellowish neutral form to green and blue oxidized forms at applied potentials ranging from 0.0 to 1.3 V.

Introduction

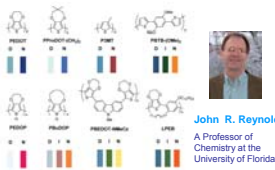
What is Electrochromism ?



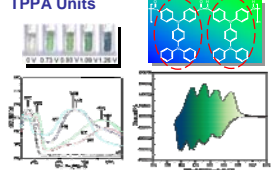
Where the switching of redox states generates new or different visible region bands, the material is said to be electrochromic.¹



Electroactive Conducting Polymers



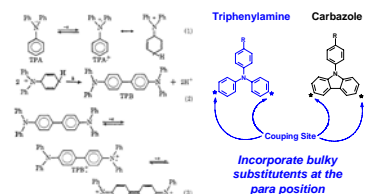
Electrochromic Polyamide with TPPA Units



John R. Reynolds
A Professor of Chemistry at the University of Florida

G.-S. Liou, S.-H. Hsiao et al. *J. Mater. Chem.*, 2005, 15, 1812.

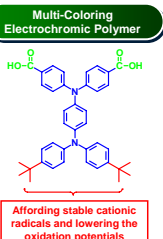
Mechanism of tail-to-tail coupling reaction of TPPA



R.N. Adams et al. *JACS*, 1966, 88, 3498.

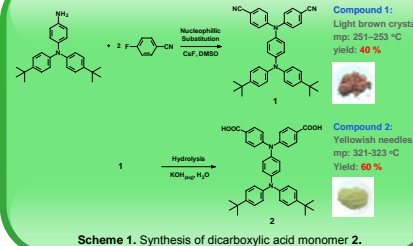
J. Ambrose et al. *J. Electrochem. Soc.*, 1975, 122, 876.

Molecular Design



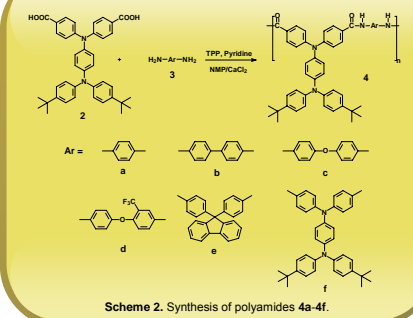
Experimental

Monomer Synthesis



Scheme 1. Synthesis of dicarboxylic acid monomer **2**.

Polymer Synthesis



Scheme 2. Synthesis of polyamides **4a-4f**.

Structural Characterization

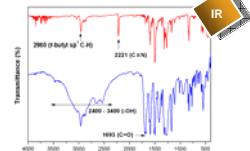


Fig. 1 IR spectra of the synthesized diimide compound **1** and diacid monomer **2**.

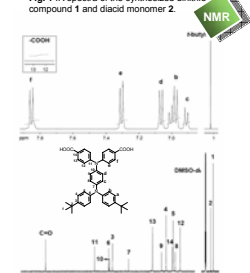


Fig. 2 (a) ¹H NMR spectrum and (b) ¹³C NMR spectrum of diacid monomer **2** in DMSO-*d*₆.



Fig. 3 Molecular structure of dicarboxylic acid monomer **2** by single crystal X-ray analysis.

Results and Discussion

Inherent Viscosity and Solubility Behavior

Polymer Code	η_{inh}^a (dL/g)	Solubility in various solvents ^b					
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
4a	—	±	±	±	±	±	±
4b	0.80	++	++	++	±	±	±
4c	—	++	±	±	±	±	±
4d	0.57	++	++	++	+	+	++
4e	0.35	++	++	++	+	+	++
4f	0.33	++	++	±	±	±	±

^a Measured at a polymer concentration of 0.5 g/dL in DMAc-5 wt % LiCl at 30 °C. ^b The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. Notation: ++, soluble at room temperature, +, soluble on heating, ±, partially soluble, —, insoluble even on heating.

Thermal Properties

Polymer Code	T_g (°C) ^a	T_d at 10 wt% (°C) ^b		Char yield (wt %) ^c
		In N ₂	In air	
4a	293	519	458	62
4b	287	532	513	63
4c	285	526	445	57
4d	287	522	499	59
4e	285	515	509	59
4f	265	540	542	60

^a Midpoint temperature of the baseline shift on the second DSC heating trace rate of 20 °C/min of the sample after quenching from 350 °C to 30 °C. ^b (rate = 20 °C/min) in nitrogen. ^c Decomposition temperature. ^d Residual weight percentage at 800 °C in nitrogen. ^e Residual weight percentage at 800 °C in air.

UV Absorption and Fluorescence

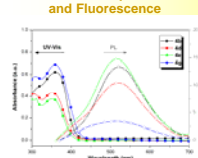


Fig. 5 UV-Vis absorption and PL spectra of the dilute solutions of polyamides **4b**, **4d**, **4e** and **4f** in NMP (1 × 10⁻⁴ M).

Photographs of Polyamides by UV Irradiation



Fig. 6 Photographs of some polyamide solutions (10⁻⁴ M) and thin films (thickness: 1–3 μm) by UV irradiation (excited at 365 nm).

Optical and Electrochemical Properties

Polymer Code	In solution						As film						Oxidation (V): vs. Ag/AgCl in CH ₃ CN				HOMO ^e (eV)		LUMO ^f (eV)	
	Abs	PL	Φ_f	λ_{max}	Abs	PL	1st		2nd		3rd		4th		E_{onset}^g	$E_{1/2}$	E_{onset}^g	$E_{1/2}$		
	λ_{max} (nm) ^a	λ_{max} (nm) ^a	(%) ^b	(nm)	λ_{max} (nm)	λ_{onset} (nm)	E_{onset}	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	(eV)	(eV)	(eV)	(eV)		
4b	361	519	0.62	429	320	420	0.58	0.69	1.07	—	—	—	—	2.95	4.94	5.05	1.99	2.10		
4d	352	521	0.69	429	301	429	0.515	0.60	0.72	1.08	—	—	—	2.89	4.96	5.08	2.07	2.19		
4e	351	517	1.08	409	310	414	0.507	0.61	0.70	1.08	—	—	—	2.99	4.97	5.06	1.98	2.07		
4f	359	515	0.15	422	309	432	0.498	0.45	0.57	0.76	0.93	1.08	2.87	4.81	4.93	1.94	2.06			
4'd	347	497	0.68	421	301	424	0.501	0.65	0.76	1.13	—	—	—	2.92	5.01	5.12	2.09	2.20		

^a Measured in dilute solutions at a concentration of 10⁻⁴ mol/L in NMP. ^b The quantum yield was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_f = 54.6\%$). ^c Oxidation potentials from cyclic voltammograms. ^d Energy gap = 1240/Abs λ_{onset} of the polymer film. ^e The HOMO energy levels were calculated from $E_{1/2}$ or E_{onset} and were referenced to ferrocene (4.8 eV; onset = 0.36 V). ^f LUMO = HOMO - E_g .

Cyclic Voltammograms of Polyamides 4d & 4'd

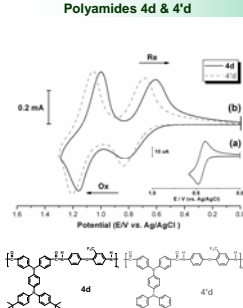


Fig. 7 Cyclic voltammograms of (a) ferrocene and (b) the cast films of polyamides **4d** and **4'd** on the ITO-coated glass slide in CH₃CN containing 0.1 M TBAP at a scan rate of 0.05 V/s.

3-D Spectroelectrochemical Behavior

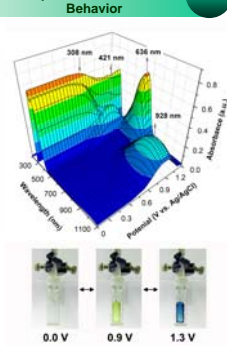


Fig. 8 3-D spectroelectrochemical behavior of the **4d** thin film on the ITO-coated glass substrate in CH₃CN with 0.1 M TBAP as the supporting electrolyte from 0 to 1.3 V vs. Ag/AgCl.

Multiple-color Electrochromic Absorption Spectra

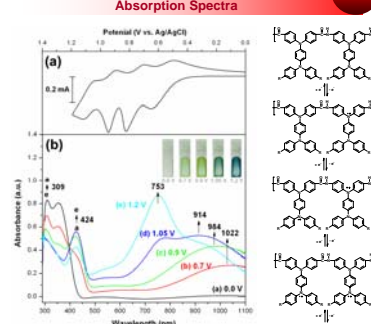


Fig. 9 (a) Cyclic voltammograms of the cast film of polyamide **4f** on the ITO-coated glass slide in CH₃CN containing 0.1 M TBAP at scan rate of 0.05 V/s. (b) Electronic absorption curves of the film of polyamide **4f** in CH₃CN with 0.1 M TBAP as the supporting electrolyte at various applied voltages: (a) 0.0, (b) 0.7, (c) 0.9, (d) 1.05 and (e) 1.20 V vs. Ag/AgCl.

Conclusion

A series of novel aromatic polyamides bearing with *N,N*-diphenyl-*N',N'*-di-4-*tert*-butylphenyl-1,4-phenylenediamine moieties were readily prepared from dicarboxylic acid **2** with various aromatic diamines via the phosphorylation polyamidation reaction. The polyamides exhibited high thermal stability, and most of them could be easily processed to strong and flexible films via solvent-casting. The polymer films had salient properties such as high robustness and stability with well-defined reversible redox couples along with a multi-electrochromic behavior. The results indicate that these polyamides are promising hole-transporting materials for OLEDs and active materials for electrochromic devices.

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Novel Aromatic Polyamides with Chromophoric *N,N*-Diphenyl-*N',N'*-di(4-*tert*-butylphenyl)-1,4-phenylenediamine Moieties: Synthesis, Luminescence, and Electrochromism

NSC 97-2221-E-027-113-MY3

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Abstract

A new class of electroactive polyamides with di-*tert*-butyl-substituted *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine (TPPA) units were prepared *via* the direct phosphorylation polycondensation of a new dicarboxylic acid monomer, *N,N*-bis(4-carboxyphenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine (**2**), with various aromatic diamines. These polyamides were amorphous with good solubility in many organic solvents, such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), and could be solution-cast into flexible polymer films. The polyamides exhibited good thermal stability with glass-transition temperatures in the range of 265–293°C and 10% weight-loss temperatures in excess of 509°C. The dilute solutions of these polyamides in NMP exhibited strong absorption bands centered at 351–361 nm and showed a green-yellow photoluminescence around 507–521 nm. Cyclic voltammograms of the polyamide films on the indium-tin oxide (ITO)-coated glass substrate in 0.1 M tetrabutylammonium perchlorate (TBAP) acetonitrile solution exhibited stable and well-defined reversible redox couples during oxidative scanning. The polyamide films also showed an interesting electrochromic property with the color change from a colorless or pale yellowish neutral form to green and blue oxidized forms at applied potentials ranging from 0.0 to 1.3 V.

1. Introduction

Numerous chemical materials exhibit redox states with distinct electronic (UV/visible) absorption spectra. Where the switching of redox states generates new or different visible region bands, the material is said to be electrochromic.¹ This interesting property led to the development of many technological applications such as display panels, camouflage materials, variable reflectance mirrors, and controllable light-transmissive windows. There is a huge amount of chemical species that exhibited electrochromic properties, including both metal coordination complexes in solution and as polymer films, metal oxide films (especially tungsten oxide), viologens (4,4'-bipyridium salts; in solution and as polymer films) and conducting polymers, such as polypyrrole, polythiophene and polyaniline, as thin films. Among all of these electrochromic materials, conjugated polymers such as poly(3-alkylthiophene)s, poly(3,4-alkylenedioxythiophene)s and poly(3,4-alkylenedioxy-pyrrole)s derivatives have emerged as promising candidates for large and flexible electrochromic devices.² The use of conjugated polymers as active layers in electrochromic devices became popular because of their fast switching speeds, high optical contrasts, processibility, color tunability through structural alternations, and multichromism.

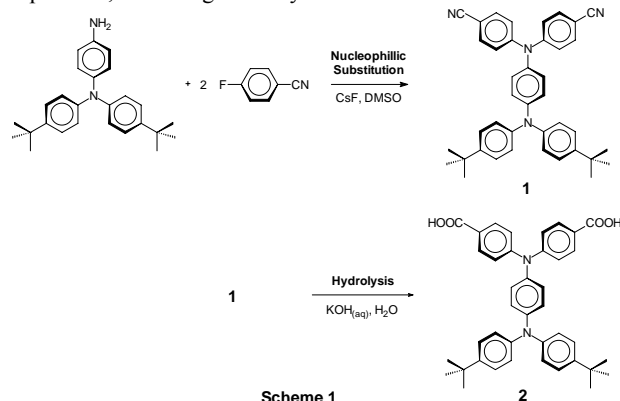
Triarylamine derivatives are well known for photo and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.³ Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylamine-based electrochromic polymers have been reported in literature. In recent years, we have developed a number of high-performance polymers (e.g., aromatic polyamides and polyimides) carrying the triarylamine unit as an electrochromic functional moiety.⁴ Our strategy was to synthesize the triarylamine-containing monomers such as diamines and dicarboxylic acids that were then reacted with

the corresponding comonomers through conventional polycondensation techniques. The obtained polymers possessed characteristically high molecular weights and high thermal stability. Because of the incorporation of packing-disruptive, three-dimensional triarylamine units along the polymer backbone, most of these polymers exhibited good solubility in polar organic solvents. They may form uniform, transparent amorphous thin films by solution casting and spin-coating methods. This is advantageous for their ready fabrication of large-area, thin-film devices.

The anodic oxidation pathways of triphenylamine derivatives were well studied.⁵ The electrogenerated cation radical of triphenylamine is not stable and could dimerize to form tetraphenylbenzidine by tail to tail coupling with loss of two protons per dimer. When the phenyl groups were incorporated by electron-donating substituents such as *tert*-butyl and methoxy groups at the *para*-position of triphenylamine, the coupling reactions were greatly prevented by affording stable cationic radicals and lowering the oxidation potentials.⁶ The redox property, electron-transfer process, and multi-coloring electrochromic behavior of the polymers bearing *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine (TPPA) segments are interesting for opto-electronic applications.⁷ In a continuation of our interest in developing electrochromic high-performance polymers having the TPPA moiety, here we synthesize a new di-*tert*-butyl-substituted TPPA-containing dicarboxylic acid, *N,N*-bis-(4-carboxyphenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine (**2**), and its derived polyamides. With such a configuration, the electrochemically active sites of the pendent phenyl groups are blocked, giving the polyamides extra redox stability. As a result, the resultant polyamides are expected to exhibit an enhanced electrochemical and electrochromic stability, which is of great importance in practical applications. Some properties of the present polyamides will be compared with those of structurally related ones derived from *N,N*-bis(4-carboxyphenyl)-*N',N'*-diphenyl-1,4-phenylenediamine (**2'**) that has been reported previously.^{4a}

2. Monomer synthesis

The new aromatic dicarboxylic acid monomer **2** was synthesized by the CsF-assisted nucleophilic substitution reaction of 4-amino-4',4''-di-*tert*-butyltriphenylamine with 4-fluorobenzonitrile, followed by alkaline hydrolysis of the intermediate dicyano compound **1**, according to the synthetic route outlined in Scheme 1.



Scheme 1

The molecular structure of the target compound **2** was confirmed by IR, NMR, and X-ray crystal analysis (Fig. 1).

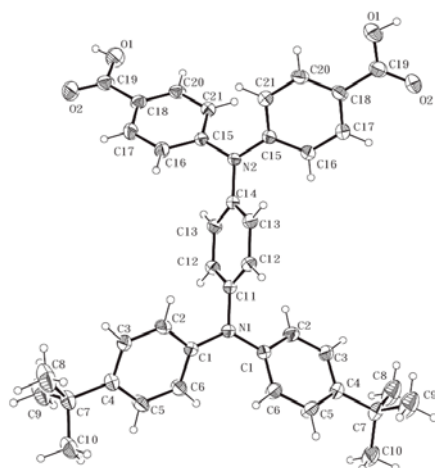
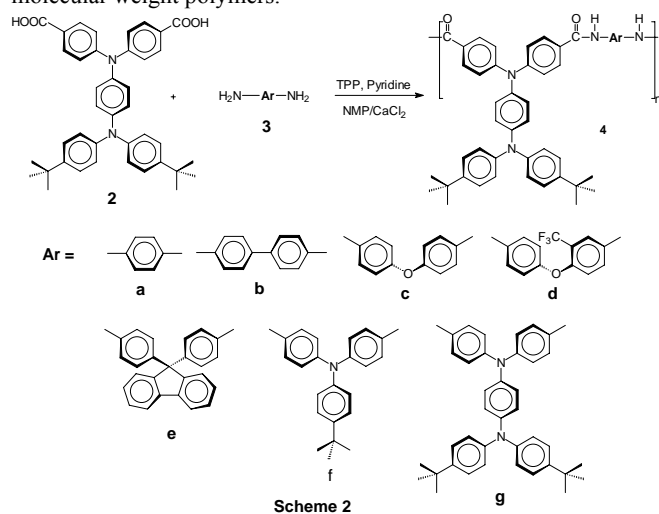


Fig. 1 Molecular structure of dicarboxylic acid monomer **2** by single crystal X-ray analysis.

3. Polymer synthesis

According to the phosphorylation polyamidation technique described by Yamazaki and coworkers,⁸ a series of novel polyamides (**4a–4g**) with di-*tert*-butyl-substituted TPPA units were synthesized from the dicarboxylic acid **2** and various diamines **3a–3g** *via* solution polycondensation using TPP and pyridine as condensing agents (Scheme 2). The obtained polyamides had inherent viscosities in the range of 0.33–0.80 dL/g and could be solution-cast into flexible and tough films, indicating high molecular weight polymers.



Scheme 2

Table 1 Inherent viscosity, solubility behavior and thermal properties of the polyamides

Polymer code	η_{inh}^a (dL/g)	Solubility in various solvents ^b						T_g (°C) ^c	T_d at 10 wt% (°C) ^d		Char yield (wt %) ^e
		NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF		In N ₂	In air	
4a	—	±	±	±	±	±	±	293	519	458	62
4b	0.80	++	++	++	±	±	—	287	532	513	63
4c	—	++	±	±	±	±	±	285	526	445	57
4d	0.57	++	++	++	+	+	++	287	522	499	59
4e	0.35	++	++	++	+	±	±	285	515	509	59
4f	0.45	++	++	+	±	±	±	279	536	532	60
4g	0.33	++	++	±	—	±	±	265	540	542	60

^a Measured at a polymer concentration of 0.5 g/dL in DMAc–5 wt % LiCl at 30 °C. ^b The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. Notation: ++, soluble at room temperature; +, soluble on heating; ±, partially soluble; —, insoluble even on heating. ^c Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 °C to 50 °C (rate = –200 °C/min) in nitrogen. ^d Decomposition temperature, recorded *via* TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm³/min. ^e Residual weight percentage at 800 °C in nitrogen.

4. Solubility and film property

The solubility behavior of polyamides was tested qualitatively, and the results are summarized in Table 1. Most of these polymers exhibited good solubility to highly polar organic solvents due to the introduction of the three-dimensional TPPA moiety and bulky pendent *tert*-butyl substituents into the repeat unit. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices. Among these polyamides, polyamide **4d** with the CF₃ substituents showed the best solubility. The result can be attributed to the bulkiness of pendent CF₃ groups which increased the disorder in the chains and hindered dense chain packing, thus, reducing the interchain interactions. It is worth noting that polyamides **4a** and **4c** formed an opaque film *via* solution casting from NMP and showed less solubility. Except for **4a** and **4c**, the other polymers could afford transparent, flexible and tough films.

5. Thermal properties

The thermal properties of the polyamides were investigated by TGA and DSC techniques. The thermal behavior data are summarized in Table 1. All the polyamides exhibited good thermal stability with no remarkable weight loss up to 450 °C in nitrogen or in air. Their decomposition temperatures (T_d) at a 10 % weight-loss in nitrogen were recorded in the range of 515–540 °C. The carbonized residue (char yield) of these aromatic polymers was more than 57 % at 800 °C in nitrogen atmosphere. The high char yields of these polymers could be ascribed to their high aromatic content. The glass-transition temperatures (T_g) of these polyamides were observed in the range of 265–293 °C by DSC. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms.

6. Optical and electrochemical properties

The optical properties of the polyamides were investigated by UV-Vis and photoluminescence (PL) spectroscopy. The results are summarized in Table 2. These polymers exhibited strong absorption bands at $\lambda_{max} = 351–361$ nm in solution and at 301–320 nm as thin films, which are mainly assignable to the combinations of $\pi-\pi^*$ and $n-\pi^*$ transitions resulting from the conjugated TPPA units. Fig. 2 shows the UV-vis absorption and PL spectra of polyamides **4b**, **4d**, **4e**, **4f**, and **4g** in NMP (concentration: 1×10^{-5} mol/L). Their PL spectra in dilute NMP solution showed maximum bands around 507–521 nm in the green region with quantum yields ranging from 0.15% to 1.08%. In the solid-state PL spectra, the polyamides exhibited fluorescence emission at 498–507 nm. The polymer films were measured for optical transparency using UV-vis spectroscopy, and the cutoff wavelengths (absorption edge; λ_0) were recorded in the range of 409–429 nm. In general, these polyamide films revealed a light color and high optical transparency.

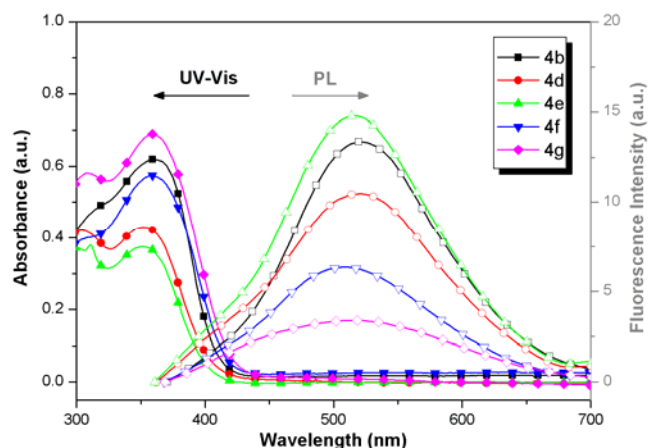


Fig. 2 UV-Vis absorption and PL spectra of the dilute solutions of polyamides **4b**, **4d**, **4e**, **4f**, and **4g** in NMP (1×10^{-5} M).

The electrochemical behavior of this series polyamides was investigated by cyclic voltammetry (CV) conducted for the cast film on the ITO-coated glass substrate as the working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The representative cyclic voltammograms for polyamides **4d** (with the *tert*-butyl substituents on the TPPA unit) and **4'd** (without the *tert*-butyl substituents on its TPPA unit) are illustrated in Fig. 3 for comparison. There are two reversible oxidation redox couples at $E_{1/2}$ values (half-wave potentials) of 0.72 ($E_{\text{onset}} = 0.60$ V) and 1.08 V for polyamide **4d** and 0.76 ($E_{\text{onset}} = 0.65$ V) and 1.13 V for polyamide **4'd** in the oxidative scan. Because of the good stability of the films and

excellent adhesion between the polymer and ITO substrate, these polyamides exhibited good reversibility of electrochromic characteristics by continuous ten cyclic scans between 0.0 and 1.3 V, changing color from the original pale yellowish to green, and then to blue upon electrochemical oxidation of the TPPA unit in the polymer chain. The first electron removal for polyamide **4d** is assumed to occur at the nitrogen atom on the pendent 4,4'-di-*tert*-butyldiphenylamine groups, which is more electron-rich than the nitrogen atom on the main-chain triphenylamine group. Comparing the electrochemical data, it could be found that polyamide **4d** is more easily being oxidized than its analogous polyamide **4'd** (0.60 vs. 0.65 V). The introduction of bulky and electron-donating *tert*-butyl group not only greatly prevents the coupling reaction but also lowers the oxidation potentials of the electroactive polyamides **4** as compared with the corresponding polyamides **4'** without the *tert*-butyl substituents. The redox potentials of the polyamides as well as their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels (below vacuum) are also listed in Table 2. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard has $E_{1/2}$ and E_{onset} of 0.44 V and 0.37 V vs Ag/AgCl in acetonitrile. Under the assumption that the HOMO level for the ferrocene standard was 4.80 eV with respect to the zero vacuum level, the HOMO levels for polyamides **4** series were evaluated to be 4.81-5.01 eV and 4.93-5.16 eV calculated from E_{onset} and $E_{1/2}$, respectively. The lower ionization potential could suggest an easier hole injection into films from ITO electrodes in electronic device applications. Traditionally, introduction of triarylamine units in conjugated polymers or organic molecules was found to effectively enhance the hole-injecting properties of the resulting materials.

Table 2 Optical and electrochemical properties of polyamides

Polymer Code	In solution			As film				Oxidation potentials (V) ^c					E_g^d (eV)	HOMO ^e (eV)		LUMO ^f (eV)	
	Abs	PL	Φ_F (%) ^b	Abs	Abs	PL	1st		2nd	3rd	4th	E_{onset}		$E_{1/2}$	E_{onset}	$E_{1/2}$	
	λ_{max} (nm) ^a	λ_{max} (nm) ^a		λ_0 (nm)	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	E_{onset}	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$	$E_{1/2}$		E_{onset}	$E_{1/2}$	E_{onset}	$E_{1/2}$
4b	361	519	0.62	429	320	420	501	0.58	0.69	1.07	—	—	2.95	4.94	5.05	1.99	2.10
4d	352	521	0.69	429	301	429	515	0.60	0.72	1.08	—	—	2.89	4.96	5.08	2.07	2.19
4e	351	517	1.08	409	310	414	507	0.61	0.70	1.08	—	—	2.99	4.97	5.06	1.98	2.07
4f	358	507	0.30	423	308	428	505	0.64	0.80	1.09	—	—	2.90	5.00	5.16	2.10	2.26
4g	359	515	0.15	422	309	432	498	0.45	0.57	0.76	0.93	1.08	2.87	4.81	4.93	1.94	2.06
4'd	347	497	0.68	421	301	424	501	0.65	0.76	1.13	—	—	2.92	5.01	5.12	2.09	2.20

^a Measured in dilute solutions at a concentration of about 10^{-5} mol/L in NMP. ^b The quantum yield was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_F = 54.6\%$). ^c Oxidation potentials from cyclic voltammograms (vs. Ag/AgCl in CH_3CN). ^d Energy gap = $1240/\text{Abs } \lambda_{\text{onset}}$ of the polymer film. ^e Calculated from $E_{1/2}$ or E_{onset} , using ferrocene (4.8 eV; onset = 0.36 V) as a standard. ^f LUMO = HOMO - E_g .

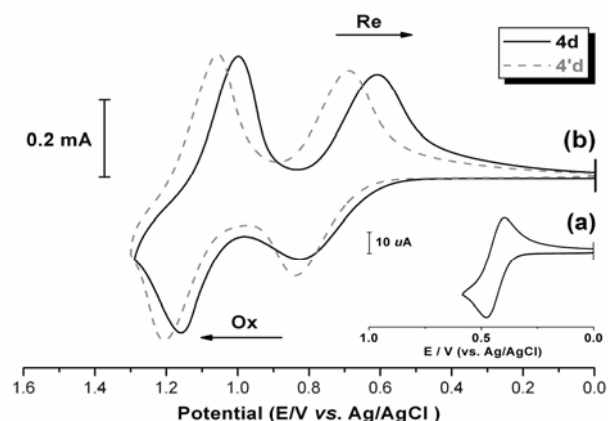


Fig. 3 Cyclic voltammograms of (a) ferrocene and (b) the cast films of polyamides **4d** and **4'd** on the ITO-coated glass slide in CH_3CN containing 0.1 M TBAP at a scan rate of 0.05 V/s.

7. Spectro-electrochemical and electrochromic properties

Spectro-electrochemical experiments were conducted to elucidate the optical characteristics of the electrochromic films. For these investigations, the polyamide film was cast on an ITO-coated glass slide (a piece that fit in the commercial UV-Vis cuvette), and a homemade electrochemical cell was built from a commercial UV-Vis cuvette. The cell was placed in the optical path of the sample light beam in a commercial diode array spectrophotometer. This procedure allowed us to obtain electronic absorption spectra under potential control in a 0.1 M TBAP/acetonitrile solution. Fig. 4 shows the three-dimensional absorbance-wavelength-applied potential correlations of polyamide **4d**. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 308 nm, characteristic for triarylamine, but it was almost transparent in the visible region. Upon oxidation of the **4d** film (increasing applied voltage from 0 to 0.9 V), the intensity of the absorption peak at 308 nm gradually decreased while a new peak at 421 nm and a broad band having its maximum absorption wavelength at 928 nm gradually increased in intensity. We attribute this spectral change to the formation of a stable monocation radical of TPPA moiety. As

the applied potential became more anodic to 1.3 V, the absorption bands of the cation radical decreased gradually in intensity, with the formation of a new broad band centered at around 636 nm. This spectral change can be attributable to the formation of dication in the TPPA segments of the polyamide. The observed UV-vis absorption changes in the film of **4b** at various potentials are fully reversible and are associated with strong color changes; indeed, they even can be seen readily by the naked eye. From the images shown in the bottom of Fig. 4, it can be seen that the film of **4d** switches from a transmissive neutral state (colorless) to a highly absorbing semi-oxidized state (green) and a fully oxidized state (blue).

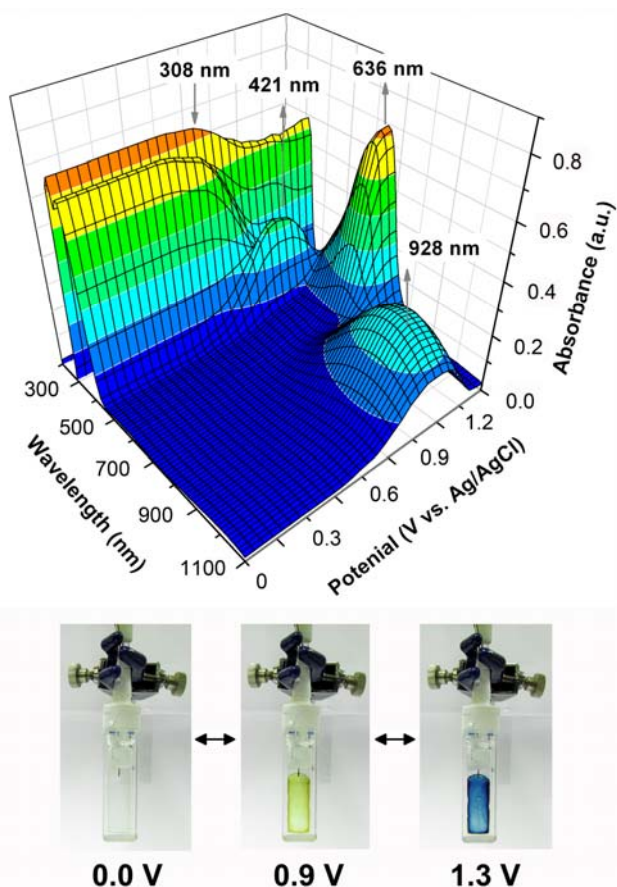


Fig. 4 3-D spectroelectrochemical behavior of the **4d** thin film on the ITO-coated glass substrate (in CH_3CN with 0.1 M TBAP as the supporting electrolyte from 0 to 1.3 V (vs. Ag/AgCl)).

The electro-optical properties of polyamide **4g** were deciphered using the changes in electronic absorption spectra upon oxidation process (see Fig. 5). Upon oxidation, the polymer film exhibited a multi-electrochromic behavior; a color change from pale yellow to green and then to blue. When the applied potentials increased positively from 0 to 0.70, 0.90, 1.05, and 1.2 V, respectively, corresponding to the first, second, third, and fourth electron oxidation, the peak of characteristic absorbance at 309 nm for neutral-form polyamide **4g** decreased gradually, while four new bands grew up at 1022, 984, 914, and 753 nm, respectively. The spectral changes are apparently arisen from the sequential oxidation processes of the nitrogen atoms in the two different TBBP segments in the main chain of this polyamide. Thus, it will be a good approach for facile color tuning of the electrochromic polyamides by incorporating TPPA units into their polymer backbones.

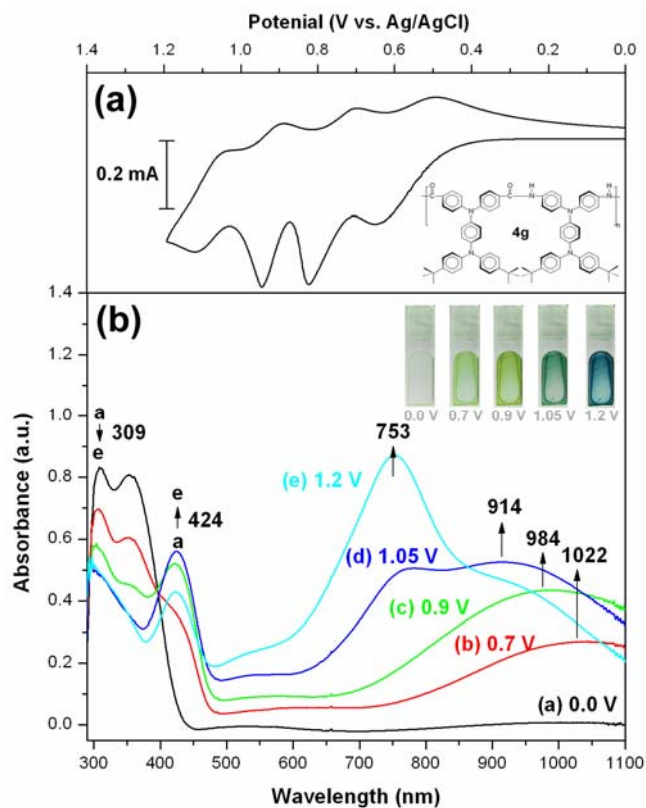


Fig. 5 (a) Cyclic voltammograms of the cast film of polyamide **4g** on the ITO-coated glass slide in CH_3CN containing 0.1 M TBAP at scan rate of 0.05 V/s. (b) Electronic absorption curves of the film of polyamide **4g** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at various applied voltages: (a) 0.0, (b) 0.7, (c) 0.9, (d) 1.05 and (e) 1.20 V (vs. Ag/AgCl).

8. Conclusions

A series of novel aromatic polyamides bearing with *N,N*-diphenyl-*N',N'*-di-4-*tert*-butylphenyl-1,4-phenylenediamine moieties were readily prepared from dicarboxylic acid **2** with various aromatic diamines *via* the phosphorylation polyamidation reaction. The polyamides exhibited high thermal stability, and most of them could be easily processed to strong and flexible films *via* solvent-casting. The polymer films had salient properties such as high robustness and stability with well-defined reversible redox couples along with a multi-electrochromic behavior. It is to be hoped that these polyamides may find applications in material science and technology as electrochromic devices and organic light-emitting diodes.

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