

# Synthesis, photoluminescent and electrochromic properties of new aromatic poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s derived from 4,4'-dicarboxy-4''-methyltriphenylamine

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## Abstract

A series of new poly(amine-hydrazide)s **I** were prepared from the dicarboxylic acid 4,4'-dicarboxy-4''-methyltriphenylamine with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH), respectively, via the Yamazaki phosphorylation reaction. Polymers **I** were readily soluble in many common organic solvents, and could be solution cast into transparent, tough, and flexible films with good mechanical properties. Differential scanning calorimetry (DSC) indicated that the hydrazide polymers had  $T_g$ 's in the range of 222–223 °C and could be thermally cyclodehydrated into the corresponding oxadiazole polymers in the range of 300–400 °C. The resulting poly(amine-1,3,4-oxadiazole)s **II** exhibited  $T_g$ 's in the range of 269–283 °C, 10% weight-loss temperatures in excess of 511 °C, and char yield at 800 °C in nitrogen higher than 63%. These poly(amine-hydrazide)s **I** exhibited strong UV–Vis absorption bands at 351–355 nm in NMP solution. Their photoluminescence spectra in NMP solution and film showed maximum bands around 459–461 nm in the blue region for **I** series. The hole-transporting and electrochromic properties are examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine-hydrazide)s **I** prepared by casting polymer solution onto an indium-tin oxide (ITO)-coated glass substrate exhibited one reversible oxidation redox couples at 1.32–1.33 V vs. Ag/AgCl in acetonitrile solution. All obtained poly(amine-hydrazide)s **I** revealed excellent stability of electrochromic characteristics, changing color from original pale yellowish to blue.

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## 1. Introduction

Recently, the use of conjugated polymers in polymer light-emitting diodes (LEDs), has received

a great deal of concern in academia and the optoelectronic industry because of their several appealing advantages over other technologies. Electron-deficient oxadiazole units have been found to be efficient in promoting electron-transporting property when incorporated into conjugated polymer main chain or attached as side groups. Thus,

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1,3,4-oxadiazole-containing conjugated polymers have been widely investigated and applied as electron-transporting or emission layers in LEDs [1–4]. Unfortunately, aromatic polyoxadiazoles are difficult to process owing to their infusible and insoluble properties and their tendency to be brittle. Many efforts have been made to improve the solubility and lower the  $T_g$ , hence to make such polymers more easily processable, for example by incorporating flexible linkages in the backbone or bulky pendant group on the aromatic rings [5–11]. 1,3,4-oxadiazole derivatives, such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), is commonly used as electron-transporting layer in the organic light-emitting diodes (OLEDs) but the efficiency was limited due to their crystallization during the operation of LED. This problem was mitigated by incorporating the electron-transporting units into the main chain or as pendants attached to the backbone of a polymer [12–14]. In addition, 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 [15–19]. Correlative polymers have also been paid increasing attention because of their unique optical properties and strong hole-transporting ability in optoelectronic devices [20–26].

Several different reaction pathways have been developed to prepare poly(1,3,4-oxadiazole)s. The most popular synthesis involves the preparation of a precursor polyhydrazide by the reaction of a diacyl chloride or derivative with hydrazine or a dihydrazide compound. This precursor polyhydrazide is cyclized to the polyoxadiazole by heating to 250–350 °C under vacuum [25] or heating in a dehydrating solvent such as sulfuric acid, polyphosphoric acid, or phosphoryl chloride [26–28].

This article reports the synthesis of a series of novel triphenylamine-containing poly(amine-hydrazide)s bearing pendent methyl groups based on dicarboxylic acids, 4,4'-dicarboxy-4''-methyltriphenylamine. The general properties such as solubility, crystallinity, thermal, and mechanical properties are reported. The electrochemical, electrochromic, and photoluminescence properties of these polymers prepared by casting solution onto an indium-tin oxide (ITO)-coated glass substrate are also described herein.

## 2. Experimental

### 2.1. Materials

4,4'-dicyano-4''-methyltriphenylamine (mp = 278–281 °C; lit [29] 188–190 °C) was synthesized by the sodium hydride assisted condensation of 4-methylaniline with 4-fluorobenzonitrile followed by the alkaline hydrolysis of the intermediate dinitrile compound [30]. *N,N*-dimethylacetamide (DMAc) (TEDIA), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), pyridine (Py) (TEDIA), and diphenyl phosphite (DPP) (ACROS) were used as received. Terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) were purchased from TCI and used without further purification. Anhydrous calcium chloride ( $\text{CaCl}_2$ ) was dried under vacuum at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

### 2.2. Polymer synthesis

The phosphorylation polycondensation method was used to prepare the poly(amine-hydrazide)s presented in this study. A typical synthetic procedure for poly(amine-hydrazide) **I-TPH** is described as follows. A dried 50-mL flask was charged with 4,4'-dicarboxy-4''-methyltriphenylamine (0.35 g; 1.00 mmol), TPH (0.19 g; 1.00 mmol), NMP (1.50 mL),  $\text{CaCl}_2$  (0.10 g), diphenyl phosphite (DPP) (1 mL), and pyridine (0.5 mL). The mixture was heated with stirring at 120 °C for 5 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was poured slowly into 300 mL of methanol with stirring, giving a fibrous precipitate that was collected by filtration, washed thoroughly with hot water and methanol. Precipitations from DMAc into methanol were carried out twice for further purification. The yield was quantitative, and the inherent viscosity of the poly(amine-hydrazide) **I-TPH** was 0.42 dL/g measured in DMAc at a concentration of 0.5 g/dL at 30 °C. IR (film): 3252 (N–H), 1648  $\text{cm}^{-1}$  (C=O). ELEM. ANAL. Calcd. for  $(\text{C}_{29}\text{H}_{24}\text{N}_5\text{O}_4)_n$  (505.5) $_n$ : C, 68.90%; H, 4.59%; N, 13.85%. Found: C, 70.03%; H, 4.43%; N, 13.90%. Another poly(amine-hydrazide) was prepared by an analogous procedure.

### 2.3. Film preparation and cyclodehydration of the hydrazide polymers

A polymer solution was made by the dissolution of about 0.5 g of the poly(amine-hydrazide) 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 overnight to slowly release the solvent, and then the film was stripped off from the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 50–60 μm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

The cyclodehydration of the poly(amine-hydrazide)s to the corresponding poly(amine-1,3,4-oxadiazole)s was carried out by heating the above fabricated polymer films under vacuum at 200 °C for 30 min, 250 °C, 300 °C, and 350 °C for 1 h, respectively.

## 3. Results and discussion

### 3.1. Polymer synthesis

A two-step procedure was employed to obtain the poly(amine-1,3,4-oxadiazole)s from 4,4'-dicarboxy-4''-methyl-triphenylamine with TPH and IPH (Scheme 1). The first stage consists of the synthesis of hydrazide prepolymers which were converted to

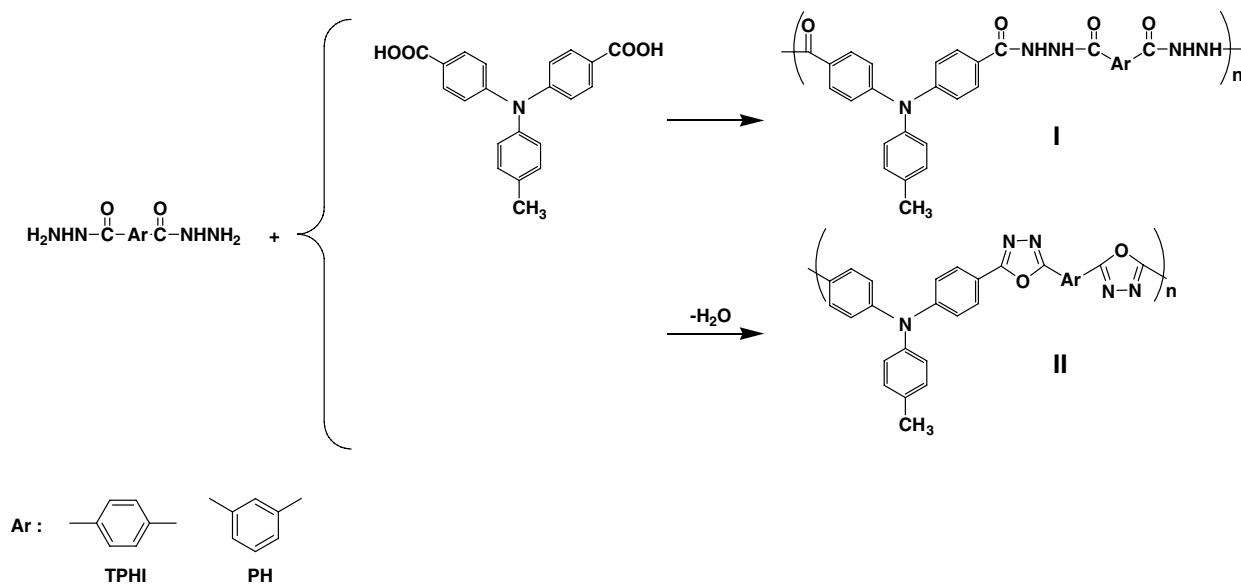
the corresponding oxadiazole polymers in the second stage by the thermal cyclodehydration of the hydrazide group into the 1,3,4-oxadiazole ring. The polymerization proceeded homogeneously throughout the reaction and afforded clear and viscous polymer solutions. All the hydrazide prepolymers precipitated in a fiber-like form when slowly pouring the resulting polymer solutions into methanol. The obtained poly(amine-hydrazide)s **I** had inherent viscosities in the range of 0.31–0.42 dL/g, and the results of elemental analysis were summarized in Table 1.

Thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring could be monitored with FTIR. As a representative study, a thin-film sample

Table 1  
Inherent viscosity and elemental analysis of poly(amine-hydrazide)s

poly(amine-amide)s		Elemental analysis (%) of poly(amine-amide)s				
Code	$\eta_{inh}^a$ (dL/g)	Formula (Molecular weight)	C	H	N	
<b>I-TPH</b>	0.42	$(C_{29}H_{24}N_5O_4)_n$ (505.5) <sub>n</sub>	Calcd	68.90	4.59	13.85
			Found	70.03	4.43	13.90
<b>I-IPH</b>	0.31	$(C_{29}H_{24}N_5O_4)_n$ (505.5) <sub>n</sub>	Calcd	68.90	4.59	13.85
			Found	70.87	4.46	14.05

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.



Scheme 1. Synthesis of hydrazide and oxadiazole polymers.

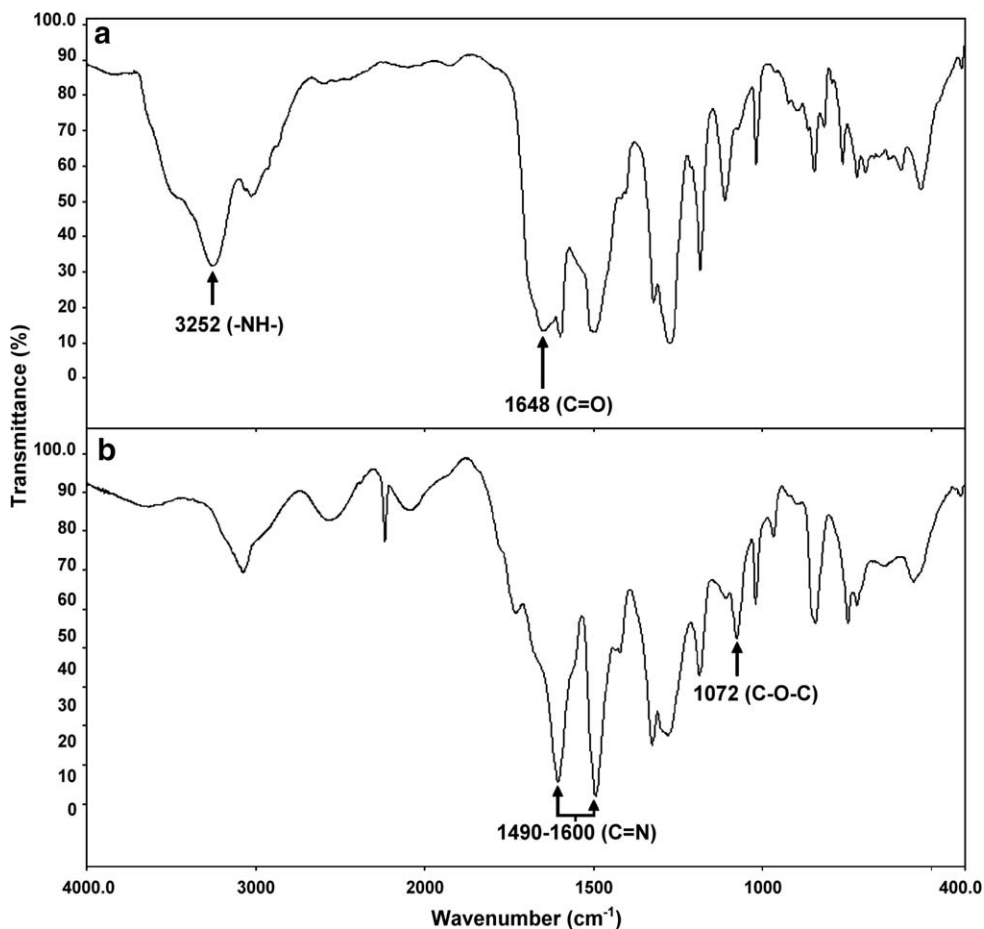


Fig. 1. IR spectra (film) of (a) poly(amine-hydrazide) **I-TPH** and (b) poly(amine-1,3,4-oxadiazole) **II-TPH**.

of polyhydrazide **I-TPH** was heated up to 350 °C for 1 h. The IR spectra of this sample are shown in Fig. 1. After heating at 350 °C for 1 h, polyhydrazide **I-TPH** was almost completely cyclized to poly(amine-1,3,4-oxadiazole) **II-TPH**, as seen by the disappearance of the N–H stretching absorption at 3252 cm<sup>-1</sup> and the carbonyl peak at 1648 cm<sup>-1</sup>. One of the characteristic bands of 1,3,4-oxadiazole ring vibration was observed at 1072 cm<sup>-1</sup> (C–O–C str.). The absorption band due to oxadiazole C=N stretching was probably buried in the strong absorption bands between 1490 and 1600 cm<sup>-1</sup> due to the skeletal vibration of benzene rings. Fig. 2 shows a typical set of <sup>1</sup>H and <sup>13</sup>C NMR spectra of poly(amine-hydrazide) **I-TPH** in DMSO-*d*<sub>6</sub>, where all the peaks have been readily assigned to the hydrogen and carbon atoms of the recurring unit. DSC was also used to investigate cyclization to the oxadiazole structure. A typical pair of DSC curves of poly(amine-hydrazide) **I-IPH** and poly-

(amine-1,3,4-oxadiazole) **II-IPH** are illustrated in Fig. 3. The main endothermic cyclodehydration reaction of the hydrazide group occurs with water evolution in the range 300–400 °C.

### 3.2. Polymer properties

#### 3.2.1. Basic characterization

From the typical diffraction patterns, the X-ray diffraction studies of the poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s indicated that all the polymers were essentially amorphous. The solubility behavior of poly(amine-hydrazide)s was tested qualitatively, and the results are presented in Table 2. All the poly(amine-hydrazide)s were highly soluble in polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and the enhanced solubility can be attributed to the introduction of

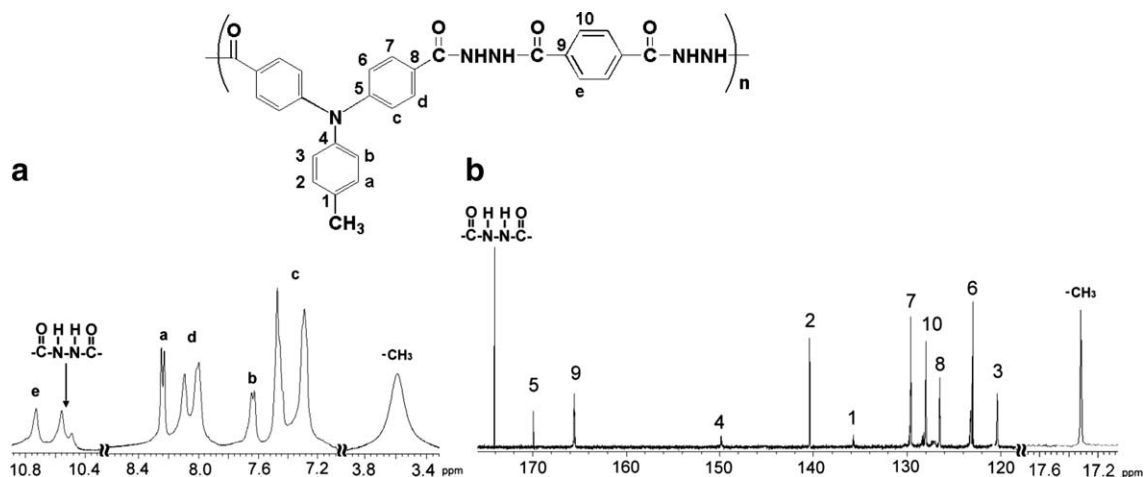


Fig. 2. (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of poly(amine-hydrazide) **I-TPH** in  $\text{DMSO-}d_6$ .

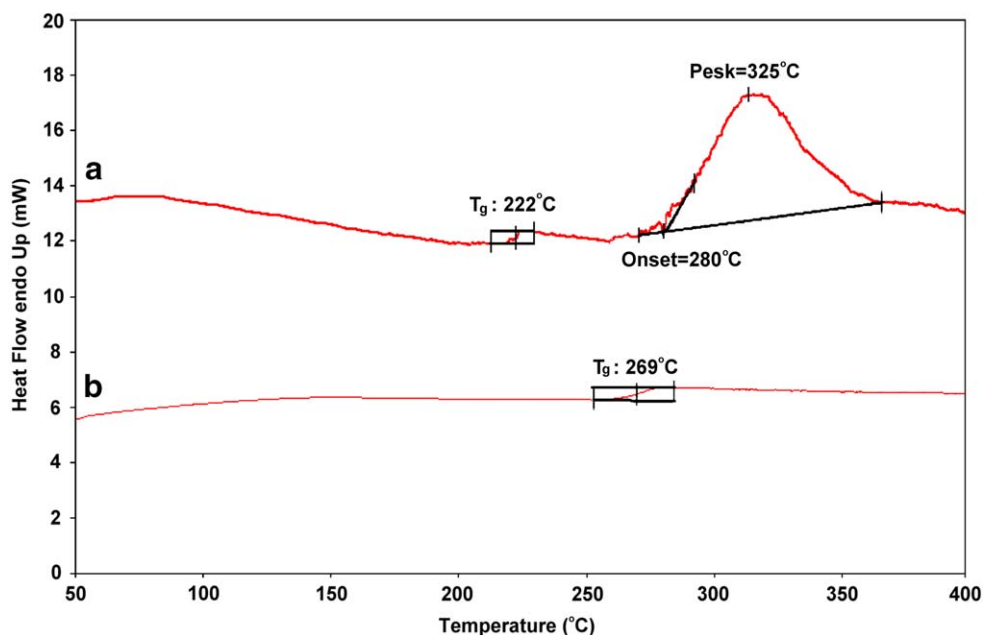


Fig. 3. DSC traces of (a) poly(amine-hydrazide) **I-IPH** and (b) poly(amine-1,3,4-oxadiazole) **II-IPH** with a heating rate of  $20\text{ }^\circ\text{C}/\text{min}^{-1}$  in nitrogen.

bulky pendent triphenylamine group in the repeat unit. Thus, the excellent solubility makes these polymers as potential candidates for practical applications by spin- or dip-coating processes.

All the aromatic poly(amine-hydrazide)s could afford flexible and tough films. These films were subjected to tensile testing, and the results are given in Table 2. The tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 69–73 MPa, 4.6–5.3% and 2.2–2.3 GPa, respectively.

DSC and TGA were used to evaluate the thermal properties of all the hydrazide and oxadiazole polymers, and the result are summarized in Table 3. These hydrazide polymers showed a distinct  $T_g$  centered in the range 222–223  $^\circ\text{C}$ . As can be seen from the DSC thermograms, all the hydrazide polymers were almost completely converted to the corresponding oxadiazole polymers when heated to 400  $^\circ\text{C}$  at a scan rate 20  $^\circ\text{C}/\text{min}$  in nitrogen. Because of the increased chain rigidity, all the oxadiazole

Table 2  
Solubility and mechanical properties of poly(amine-hydrazide)s films

Polymer	Solvent <sup>a</sup>						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl <sub>3</sub>
<b>I-TPH</b>	++	++	++	++	++	–	–
<b>I-IPH</b>	++	++	++	++	++	–	–

Polymer	Tensile strength (MPa)		Elongation at break (%)		Initial modulus (GPa)	
<b>I-TPH</b>	69		4.6		2.3	
<b>I-IPH</b>	73		5.3		2.2	

<sup>a</sup> Solubility: ++, soluble at room temperature; +, soluble on heating; –, insoluble even on heating.

Table 3  
Thermal behavior data of aromatic poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s

Polymer <sup>a</sup>	$T_g$ (°C)	$T_o$ (°C)	$T_p$ (°C)	
<b>I-TPH</b>	223	285	297	
<b>I-IPH</b>	222	280	325	

Polymer	$T_g$ (°C) <sup>b</sup>	$T_d$ at 5% weight loss (°C) <sup>c</sup>		$T_d$ at 10% weight loss (°C) <sup>c</sup>		Char yield (wt% <sup>d</sup> )
		N <sub>2</sub>	Air	N <sub>2</sub>	Air	
<b>II-TPH</b>	283	485	482	511	508	63
<b>II-IPH</b>	269	497	486	518	511	63

<sup>a</sup> DSC data obtained from the second DSC heating traces with a heating rate 20 °C min<sup>-1</sup>. The samples were first heated to 250 °C and then cooling down to 50 °C at 200 °C min<sup>-1</sup>.  $T_g$ : the midpoint of baseline shift on the DSC curve;  $T_o$ : extrapolated onset temperature of the endotherm peak;  $T_p$ : endotherm peak temperature.

<sup>b</sup> Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C /min) of the sample after quenching from 400 °C.

<sup>c</sup> Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm<sup>3</sup>/min.

<sup>d</sup> Residual weight percentage at 800 °C in nitrogen.

polymers showed increased  $T_g$  values in comparison with the corresponding hydrazide polymers; their  $T_g$ 's stayed between 270 and 285 °C. All the oxadiazole polymers exhibited good thermal stability because no significant weight losses were observed up to 400 °C in nitrogen. The 10% weight-loss temperatures of the poly(amine-1,3,4-oxadiazole)s in nitrogen and air were recorded in the range of 511–518 °C and 508–511 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 63% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content.

### 3.2.2. Optical and electrochemical properties

The optical and electrochemical properties of the poly(amine-hydrazide)s were investigated by cyclic voltammetry, UV–Vis and photoluminescence spectroscopy. The results are summarized (Table 4). These hydrazide polymers UV/vis absorption measurements in NMP solution and film exhibited strong UV–Vis absorption bands at 348–350 nm, assignable to the  $\pi$ – $\pi^*$  transition resulting from the conjugation between the aromatic rings and nitrogen atoms. UV–Vis absorption and photoluminescence spectra of poly(amine-hydrazide)s **I** series are shown in Fig. 4. Their photoluminescence spectra in NMP solution showed maximum bands around 458–459 nm in the blue region. The optical transparency of polymer films was measured using UV–Vis transmission spectroscopy, and the cutoff wavelengths (absorption edge;  $\lambda_0$ ) of poly(amine-hydrazide) **I** and poly(amine-1,3,4-oxadiazole) **II** films in the range of 423–462 nm from the UV–Vis spectra are also indicated in Fig. 5. The redox behavior of poly(amine-hydrazide)s **I** series was investigated by cyclic voltammetry conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH<sub>3</sub>CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for poly(amine-hydrazide)s **I** are shown in Fig. 6. There are one reversible oxidation redox couples at  $E_{1/2} = 1.32$  V for poly(amine-hydrazide) **I-TPH** and one reversible oxidation redox couple at  $E_{1/2} = 1.33$  V for poly(amine-hydrazide) **I-IPH** in the oxidative scan. The energy of the HOMO and LUMO levels of the investigated poly(amine-hydrazide)s can be determined from the oxidation half-wave potentials and the onset absorption wavelength and the results were listed in Table 4. For example (Fig. 6), the oxidation onset potential for poly(amine-hydrazide) **I-TPH** has been determined

Table 4  
Optical and electrochemical properties for the aromatic poly(amine-hydrazide)s and poly(amine-1,3,4-oxadiazole)s

Index	$\lambda_0$ (nm) <sup>c</sup>	$\lambda_{\text{abs,max}}$ (nm) <sup>a</sup>	$\lambda_{\text{abs,onset}}$ (nm) <sup>a</sup>	$\lambda_{\text{PL}}$ (nm) <sup>b</sup>	Oxidation (V) (vs. Ag/AgCl)		HOMO–LUMO Gap <sup>e</sup> (eV)	HOMO <sup>f</sup> (eV)	LUMO <sup>g</sup> (eV)	$\Phi_{\text{PL}}$ <sup>h</sup> (%)
					$E_{1/2}$	$E_{\text{onset}}$				
<b>I-TPH</b>	436	355(357)	(421)	461(482)	1.32	1.08	2.95	5.44	2.49	2
<b>I-IPH</b>	423	351(357)	(419)	459(471)	1.33	1.10	2.96	5.46	2.50	14
<b>II-TPH</b>	462	– <sup>d</sup> (381)	(472)	– <sup>d</sup> (573)	– <sup>d</sup>	– <sup>d</sup>	2.63	–	–	– <sup>d</sup>
<b>II-IPH</b>	435	– <sup>d</sup> (373)	(456)	– <sup>d</sup> (567)	– <sup>d</sup>	– <sup>d</sup>	2.72	–	–	– <sup>d</sup>

<sup>a</sup> UV/vis absorption measurements in NMP ( $10^{-5}$  M) at room temperature, values in parentheses are polymer thin films.

<sup>b</sup> PL spectra measurements in NMP ( $10^{-5}$  M) at room temperature, values in parentheses are polymer thin films.

<sup>c</sup> The cutoff wavelengths ( $\lambda_0$ ) from the transmission UV/vis absorption spectra of polymer films (50–60  $\mu\text{m}$ ).

<sup>d</sup> No discernible oxidation redox was observed or poor solubility in NMP.

<sup>e</sup> The data were calculated by the equation:  $\text{gap} = 1240/\lambda_{\text{onset}}$  of polymer film.

<sup>f</sup> The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

<sup>g</sup> LUMO = HOMO – gap.

<sup>h</sup> These values were measured by using quinine sulfate (dissolved in 1 N  $\text{H}_2\text{SO}_{4(\text{aq})}$ ) with a concentration of  $10^{-5}$  M, assuming  $\Phi_{\text{PL}}$  of 0.55) as a standard at 24–25 °C [31,32].

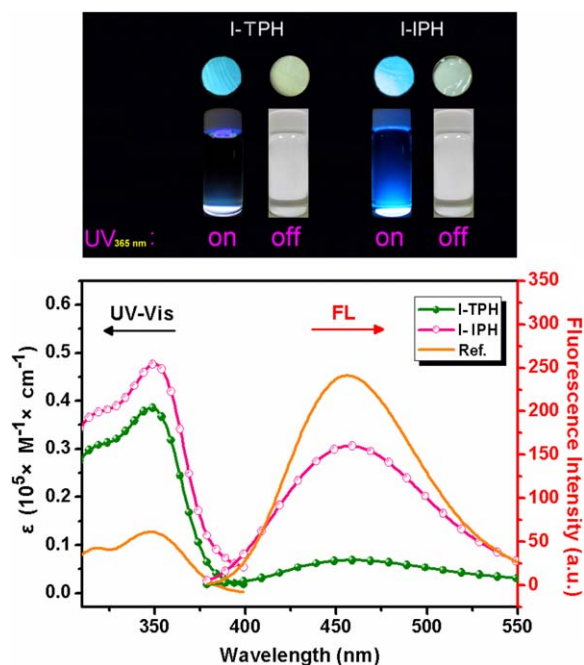


Fig. 4. Absorptions and PL spectra of poly(amine-hydrazide)s with a concentration of NMP ( $1 \times 10^{-5}$  M). Quinine sulfate dissolved in  $\text{H}_2\text{SO}_{4(\text{aq})}$  with a concentration of ( $1 \times 10^{-5}$  M), assuming  $\Phi_{\text{PL}}$  of 0.55.

as 1.08 V vs Ag/AgCl. The external ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox standard  $E_{1/2}$  ( $\text{Fc}/\text{Fc}^+$ ) is 0.44 V vs Ag/AgCl in  $\text{CH}_3\text{CN}$ . Assuming that the HOMO energy for the  $\text{Fc}/\text{Fc}^+$  standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for poly(amine-hydrazide) **I-TPH** has been evaluated to be 5.44 eV.

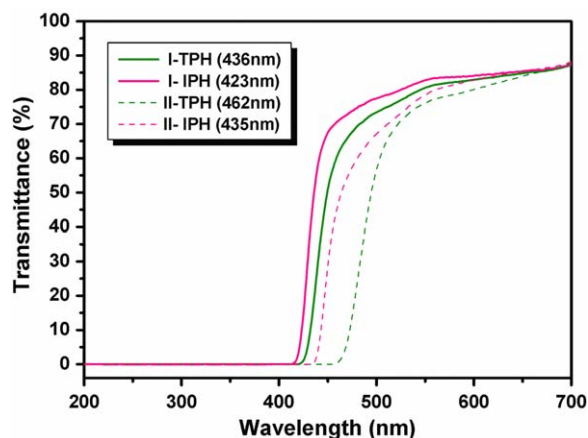


Fig. 5. Transmission UV-visible absorption spectra of polymer thin films (50–60  $\mu\text{m}$ ).

### 3.2.3. Electrochromic characteristics

Electrochromism of the thin films from poly(amine-hydrazide)s **I** was examined by casting polymer solution onto an indium-tin oxide (ITO)-coated glass substrate, and their electrochromic absorption spectra were monitored by a UV-Vis spectrometer at different applied potentials. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. The typical electrochromic absorption spectra of poly(amine-hydrazide)s **I-TPH** and **I-IPH** are shown as Figs. 7 and 8. When the applied potentials increased positively from 0.00 to 1.83 V, the peak of characteristic absorbance at 360 nm, characteristic for poly(amine-hydrazide) **I-TPH** decreased gradually while one new bands grew up at 702 nm due to

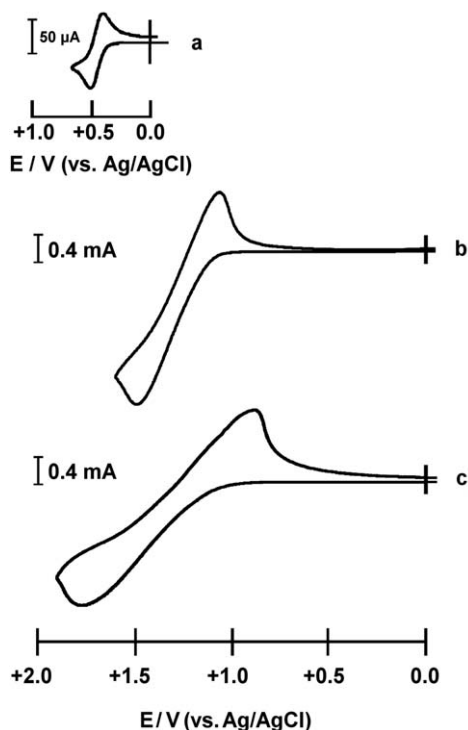


Fig. 6. Cyclic Voltammograms of (a) ferrocene, (b) poly(amine-hydrazide) **I-TPH**, and (c) poly(amine-hydrazide) **I-IPH** films onto an indium-tin oxide (ITO)-coated glass substrate in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAP. Scan rate = 0.1 V/s.

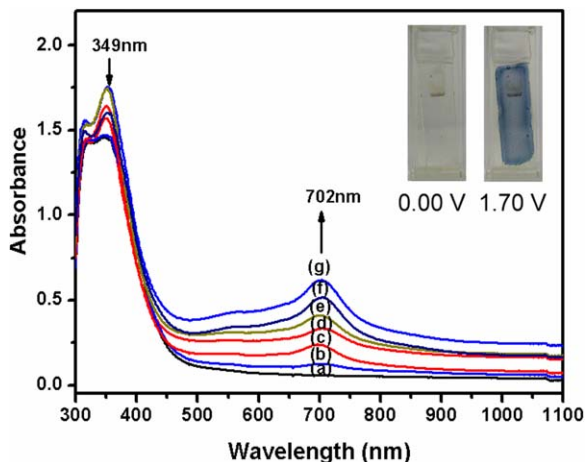


Fig. 7. Electrochromic behavior of poly(amine-amide) **I-TPH** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 1.24, (c) 1.32, (d) 1.46, (e) 1.57, (f) 1.63, and (g) 1.70 V.

the oxidation. The new spectrum was assigned as that of the cationic radical poly(amine-hydrazide)<sup>+</sup> and the film color changed into the blue (as shown

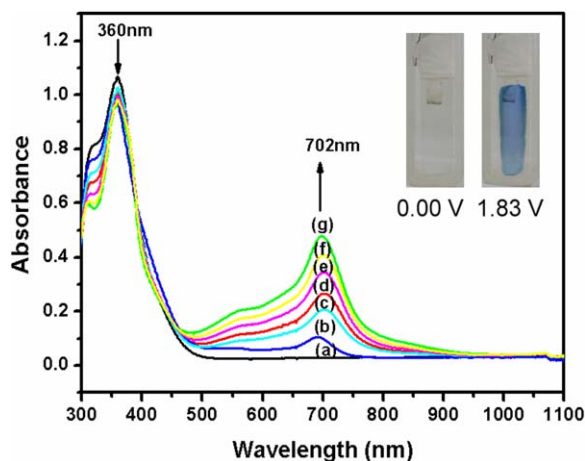


Fig. 8. Electrochromic behavior of poly(amine-amide) **I-IPH** thin film (in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP as the supporting electrolyte) at (a) 0.00, (b) 1.26, (c) 1.33, (d) 1.48, (e) 1.59, (f) 1.70, and (g) 1.83 V.

in Fig. 7). The electrochromic characteristics of poly(amine-hydrazide) **I-IPH** was also shown in Fig. 8. When the applied potential increased positively from 0.00 to 1.70 V, the absorbance at 349 nm, characteristic for poly(amine-hydrazide) **I-IPH** decreased gradually while a new bands grew up at 702 nm. The new spectrum was assigned as that of the cationic radical poly(amine-hydrazide)<sup>+</sup> and showed the complementary color of blue.

#### 4. Conclusions

A novel poly(amine-hydrazide)s **I** were prepared from the dicarboxylic acid, 4,4'-dicarboxy-4''-methyltriphenylamine, with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) by the Yamazaki phosphorylation reaction. The introduction of the bulky intrinsic electron-donating triphenylamine group could increase the HOMO energy levels and disrupt the coplanarity of aromatic units in chain packing which increases the between-chains spaces or free volume thus enhancing solubility of the formed poly(amine-hydrazide)s **I**. All the polymers were amorphous in nature as evidenced by the WAXD and DSC analysis. The poly(amine-hydrazide)s **I** revealed good stability of electrochromic characteristics, changing color from original pale yellowish to blue. Thus, our novel poly(amine-hydrazide)s have a great potential as a new type of hole-transporting and electrochromic materials due to their proper HOMO values and excellent thermal stability.



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