

Electrochemically Active Polyhydrazides and Poly(1,3,4-oxadiazole)s

Bearing Bulky Diphenylpyrenylamine Units

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Abstract

A novel class of polyhydrazides with the electroactive diphenylpyrenylamine unit were prepared from the polycondensation reactions of a newly synthesized dicarboxylic acid monomer, i.e., 1-[*N,N*-di(4-carboxyphenyl)amino]pyrene (**4**), with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) via the Yamazaki phosphorylation reaction. The hydrazide polymers could be thermally cyclodehydrated into the corresponding poly(1,3,4-oxadiazole)s in the range of 300-400 °C. All polymers exhibited good solubility in many polar organic solvents and could afford robust films via solution casting. In addition to high T_g values and good thermal stability, these polymers also showed useful HOMO energy levels, strong blue light-emitting fluorescence and interesting electrochromic characteristics.

1. Introduction

Due to the large planar conjugated aromatic characteristic, pyrene has strong π electron delocalization energy and efficient fluorescence property, and the emission is pure blue to permit ready exploitation as a blue-light emitting material in organic light emitting diodes (OLEDs).¹ Many pyrene derivatives have been used in OLEDs in order to improve hole transporting ability because of the electron-rich property of the pyrene moiety.^{2,3} However, the high tendency towards π - π stacking of the pyrene moieties generally lends the pyrene-containing 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. It has been demonstrated that the pyrenes functionalized by sterically hindered aryl rings do not undergo close π -stacking leading to solid-state emission properties that parallel those in the solution state.⁴ In addition, diarylamino functionalized pyrene derivatives have been found to perform efficiently as bright blue emitters and charge transport materials in OLEDs.⁵ Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters. 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.^{6,7}

Aromatic poly(1,3,4-oxadiazole)s have been the focus of considerable interest with regard to the production of high-performance materials, particularly owing to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring, which, from the spectral and electronic points of view, is similar to a *p*-phenylene structure.^{8,9} Recently, 1,3,4-oxadiazole-containing conjugated polymers have been widely investigated and applied as electron transport or emission layers in organic light-emitting devices.^{10,11} However, aromatic polyoxadiazoles are generally difficult to process owing to their infusible and insoluble properties and their tendency to be brittle. For the practical use in various applications, new aromatic polyoxadiazoles possessing both high thermal stability and solubility in common organic solvents have been required. 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.¹²⁻¹⁷ Our strategy was to synthesize the triarylamine-containing monomers such as diamines and dicarboxylic acids that were then reacted with the corresponding co-monomers through conventional polycondensation techniques. The obtained polymers possessed characteristically high molecular weights and high thermal stability. Because of the incorporation of packing-disruptive, propeller-shaped 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.

Herein we report the synthesis of the new dicarboxylic acid monomer **4** and their derived polyhydrazides and poly(1,3,4-oxadiazole)s containing the bulky diphenylpyrenylamine moiety. The thermal, fluorescent, electrochemical, and electrochromic properties of these polymers are also presented and compared with those of structurally related ones from 4,4'-dicarboxytriphenylamine.

2. Experimental

2.1. Synthesis of 1-[*N,N*-di(4-carboxyphenyl)amino]pyrene (**4**)

The new dicarboxylic acid monomer **4** containing a diphenylpyrenylamine unit was synthesized by the synthetic route outlined in Scheme 1. In the first step, the intermediate compound, 1-nitropyrene (**1**) was synthesized by electrophilic aromatic substitution of pyrene by using copper nitrate trihydrate as the nitration agent. Reduction of the nitro group of compound **1** by means of hydrazine and Pd/C gave 1-aminopyrene (**2**). The target dicarboxylic acid monomer **4** was prepared by alkaline hydrolysis of 1-[*N,N*-di(4-cyanophenyl)amino]pyrene (**3**) resulting from *N,N*-diarylation of compound **2** with *p*-fluorobenzonitrile in the presence of cesium fluoride (CsF). Figure 1 illustrates the ¹H NMR and ¹³C NMR spectra of the dicarboxylic acid monomer **4**. Assignments of each carbon and hydrogen are assisted by the two-dimensional (2-D) COSY NMR spectra, and these spectra are in good agreement with the proposed molecular structure of **4**.

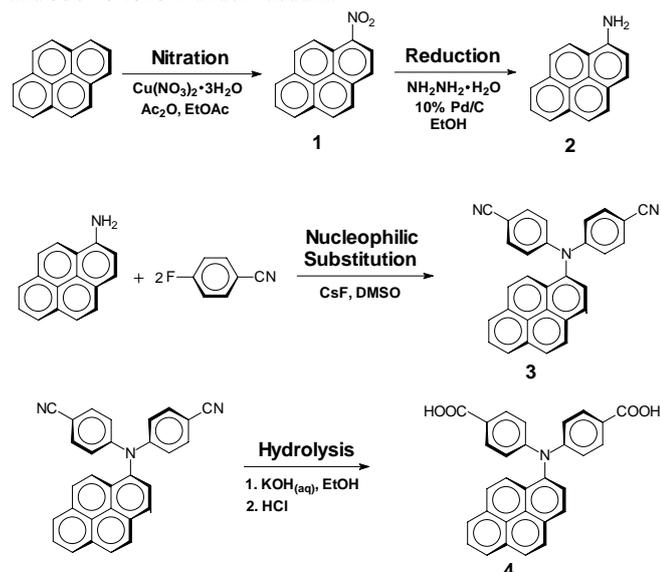
2.2. Synthesis of polyhydrazides

The synthesis of polyhydrazide **I-IPH** was used as an example to illustrate the general synthetic route used to produce the polyhydrazides. A mixture of 0.389 g (0.85 mmol) of the newly synthesized diacid monomer **4**, 0.165 g (0.85 mmol) of isophthalic dihydrazide (IPH), 0.1 g of anhydrous calcium chloride, 1.0 mL of diphenyl phosphite (DPP), 0.4 mL of pyridine, and 0.6 mL of *N*-methyl-2-pyrrolidinone (NMP) was heated with stirring at 120 °C for 5 h. The resulting polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a tough, 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 *N,N*-dimethylacetamide (DMAc)/methanol were carried out twice for further purification. The inherent viscosity of polyhydrazide **I-IPH** was 0.31 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

2.3. Film preparation and cyclodehydration of polyhydrazides

A solution of polyhydrazide was made by dissolving about 0.5 g polymer sample in 10 mL of DMAc. The homogeneous solution was poured into 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to slowly release of the solvent, and then the film was stripped off from the glass substrate and further dried in vacuum at 160 °C for 6 h. The obtained films were about 90 μm thick and were used for X-ray diffraction measurements, solubility tests, thermal analyses, optical and electrochemical properties and electrochromic characteristics measurements.

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



Scheme 1. Synthetic route to the diacid monomer **4**.

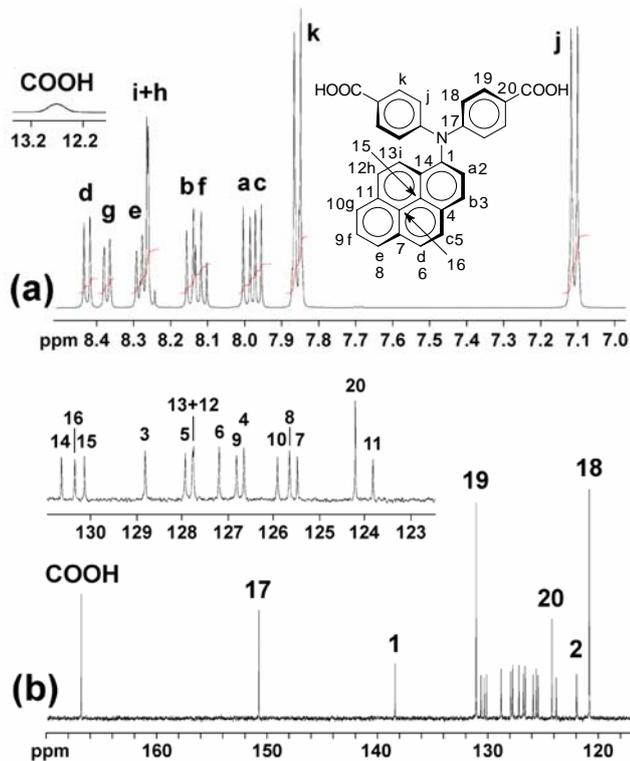
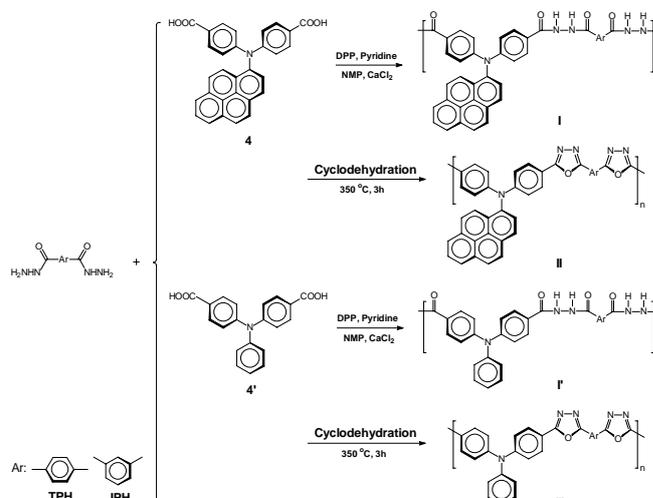


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of dicarboxylic acid monomer **4** in $\text{DMSO}-d_6$.

3. Results and discussion

3.1 Polymer synthesis

A two-step procedure was employed to obtain the poly(1,3,4-oxadiazole)s from the newly synthesized dicarboxylic acid monomer **4** with TPH and IPH by using phosphorylation technique that described by Yamazaki and co-workers¹⁸ (Scheme 2). The first stage consists of the synthesis of hydrazide prepolymers which are 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. In the first stage, the polymerization proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the hydrazide prepolymers precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions into methanol. The obtained organo-soluble polyhydrazides and poly(1,3,4-oxadiazole)s had inherent viscosities in the range of 0.22–0.38 dL/g (Table 1).



Scheme 2. Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s.

Table 1. Inherent viscosity and solubility properties of polymers

Polymer code	η_{inh}^a (dL/g)	Solubility in various solvents ^b					
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
I-TPH	0.38	++	++	++	++	+	+/-
I-IPH	0.31	++	++	++	++	+	+/-
II-TPH	0.22	++	+	+	+	+/-	-
II-IPH	0.24	++	+	+	+	+/-	-
I'-TPH	0.53	++	++	++	++	+	-
I'-IPH	0.46	++	++	++	++	+	-
II'-TPH	-	+/-	-	-	-	-	-
II'-IPH	-	+/-	-	-	-	-	-

^a Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc at 30 °C.

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

3.2. Organo-solubility and thermal properties

All the polyhydrazides and poly(1,3,4-oxadiazole)s were readily soluble in amide-type polar aprotic solvents (such as NMP, DMAc, and DMF). The high solubility of these polymers is apparently due in part to the presence of the packing-disruptive diphenylpyrenylamine unit in the polymer backbone, which resulted in increased chain packing distances and decreased intermolecular interactions.

Thermal properties of all polymers were evaluated by DSC, TMA and TGA techniques. The thermal behavior data of these polymers are summarized in Table 2. The typical experiment conditions of polyhydrazide **I-TPH** converted to poly(1,3,4-oxadiazole) **II-TPH** for the cyclization were selected on the basis of the weight loss behavior observed by dynamic TGA as shown in Figure 1. Weight loss corresponding to conversion of the polyhydrazide to the poly(1,3,4-oxadiazole) started at temperatures in the vicinity of 300 °C and continued for another 80 °C. This also

agreed quite well with the strong endothermic peak between 300-380 °C in the DSC thermogram. The glass-transition temperatures (T_g) of polyhydrazides and poly(1,3,4-oxadiazole)s were observed in the range of 218-254 and 287-304 °C by DSC. The 10 % weight-loss temperatures (T_d^{10}) of the polyoxadiazoles in nitrogen and air were recorded in the range of 517-526 °C and 527-531 °C, respectively. The amount of carbonized residue (char yield) of these polymers was more than 65 % at 800 °C in nitrogen. When compared with analogous polymers **I'** and **II'** series, the high T_g values and char yields of these polymers can be ascribed to their bulky pyrenyl moiety.

Table 2. Thermal properties of the polymers

Code	Polyhydrazides ^a			Code	Poly(1,3,4-oxadiazole) ^b			
	T_g (°C)	T_o (°C)	T_p (°C)		T_g (°C)	T_d^{10} (°C) ^c		Char yield (wt%) ^d
						N ₂	Air	
I-TPH	254	319	340	II-TPH	304	526	531	64
I-IPH	218	312	335	II-IPH	287	517	527	65
I'-TPH	196	298	324	II'-TPH	265	491	518	60
I'-IPH	181	304	338	II'-IPH	263	490	508	53

^a DSC data obtained from the DSC heating traces with a heating rate of 20 °C/min in nitrogen. T_g : the midpoint of baseline shift on the first DSC trace; T_o : extrapolated onset temperature of the endothermic peak; T_p : endothermic peak temperature.

^b The polymer film samples were heated at 300 °C for 1 hr prior to all the thermal analyses.

^c Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

^d Residual weight percentages at 800 °C under nitrogen flow.

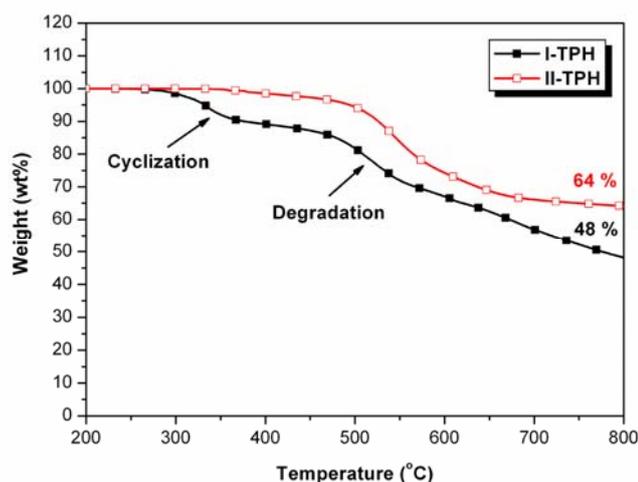


Figure 1. TGA curves of polyhydrazide **I-TPH** and poly(1,3,4-oxadiazole) **II-TPH** with heating rate of 20 °C/min in nitrogen.

3.3 Absorption and fluorescence

The optical properties of all the polymers were investigated by UV-vis and photoluminescence (PL) spectroscopy. The results are summarized in Table 3. These polymers exhibited UV-Vis absorption maxima at 332~397 nm in NMP solutions, assignable to the combinations of $n-\pi^*$ and $\pi-\pi^*$ transitions in the conjugated diphenylpyrenylamine unit. Figure 2 shows the UV-Vis absorption and photoluminescence (PL) spectra of polyhydrazides and poly(1,3,4-oxadiazole)s in NMP solutions (10^{-5} mol/L). The diphenylpyrenylamine-based polyhydrazides **I-TPH**, **I-IPH** and poly(1,3,4-oxadiazole) **II-IPH**, exhibited sky blue fluorescence emission maximum between 457~470 nm in NMP solution with quantum yield (Φ_{PL}) of 15.8, 65.8 % and 27.2 %, respectively. Less fluorescence efficiency of the polymers derived from TPH as compared to those from IPH might be attributed to the quenching effect arising from interchain charge transfer. Larger Stokes shift for the polyoxadiazole **II-TPH** might be explained by its longer conjugation length in the backbone. The decreased Φ_{PL} of the polyoxadiazoles **II** with respect to polyhydrazides **I** also could be attributable to the quenching effect caused by the intermolecular

charge transfer between the diphenylpyrenylamine donor and the oxadiazole acceptor.

Table 3. Optical properties of the polymers

Polymer code	In solution			As film (nm)	
	Abs λ_{max} (nm) ^a	PL λ_{max} (nm) ^b	Φ_{PL} (%) ^c	Abs λ_{max} (nm)	Abs λ_{onset} (nm)
I-TPH	332	457	15.8	372	446
I-IPH	332	457	65.8	359	434
II-TPH	397	545	2.20	396	396
II-IPH	380	470	27.2	385	385
I'-TPH	354	502	20.4	359	428
I'-IPH	364	462	65.0	357	413
II'-TPH	389	518	10.1	391	444
II'-IPH	383	462	30.8	381	432

^a UV/vis absorption measured in NMP (10^{-5} mol/L) at room temperature.

^b PL spectra measurements were excited at absorption λ_{max} in NMP (10^{-5} mol/L) at room temperature.

^c The quantum yield was measured by using 9,10-diphenylanthracene (dissolved in cyclohexane with a concentration of 10^{-5} M, assuming photoluminescence quantum efficiency of 95%) as a standard at room temperature.

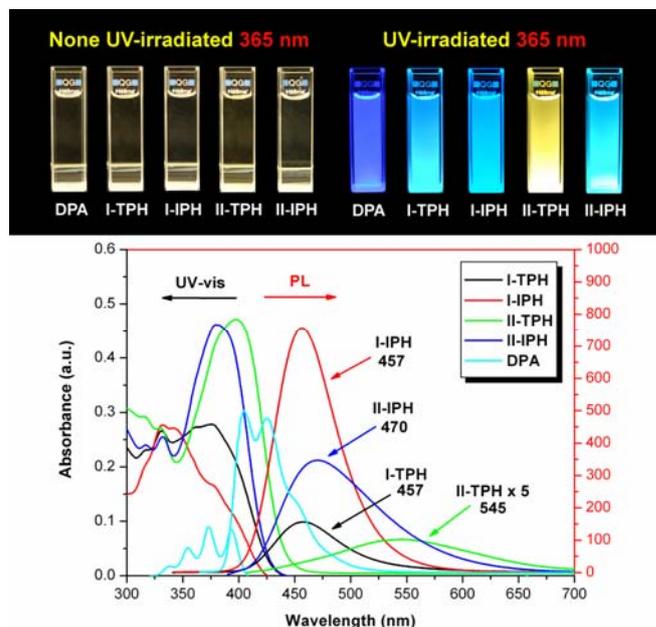


Figure 2. UV-Vis absorption and PL spectra of the dilute solutions of the prepared polymers in NMP (10^{-5} M). A solution of 9,10-diphenylanthracene (DPA) dissolved in cyclohexane (10^{-5} M) was used as the standard. ($\Phi_{PL} = 90\%$). Photographs show the appearance of these polymer solutions before and after exposure to a standard laboratory UV lamp (Excited at 365 nm).

3.4 Electrochemical properties

We undertook a study of the redox behaviors of all the synthesized the electroactive polymers by using cyclic voltammetry (CV). Electrochemical technique was conducted for a cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) or N,N -dimethylformamide (DMF) containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated Ag/AgCl as reference electrode under nitrogen atmosphere. The results are summarized in Table 4. There is an irreversible anodic redox couple and a reversible cathodic redox couple observed on the CV scans of all polymers. Figure 3 shows the typical cyclic voltammograms for the representative poly(1,3,4-oxadiazole) **II-TPH**. This polymer started oxidation at around 1.12 V (vs Ag/AgCl), but this oxidation process is irreversible. Two reversible reduction processes were observed for **II-TPH**; the first and second stage reduction stage could be assigned to the pyrenyl and oxadiazole group, respectively.

These polymers exhibited oxidation onset and reduction onset potentials (E_{onset}) in the ranges of 1.08~1.12 V and -1.37~-1.86 V, respectively, according to their CV curves. The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the corresponding polymers can be determined from the oxidation and reduction onset potentials (E_{onset}) and absorption onset wavelength. Assuming that the HOMO energy level for the ferrocene/ferrocenium (Fc/Fc^+) standard is 4.80 eV with respect to the zero vacuum level, the HOMO and LUMO energy level for polyhydrazide **I-TPH** has been calculated to be -5.44 and -2.52 eV. The HOMO and LUMO energy levels of poly(1,3,4-oxadiazole) **II-TPH** was also determined to be -5.47 and -2.99 eV.

Table 4. Redox potentials and energy levels of the polymers

Polymer code	Oxidation (V) ^a	Reduction (V) ^b		E_{g}^{EC} (eV) ^d	$E_{\text{g}}^{\text{opt}}$ (eV) ^e	$E_{\text{HOMO/LUMO}}$ (eV) ^f
	E_{onset}	$E_{1/2}$ ^c	E_{onset}			
I-TPH	1.08	-1.95	-1.84	2.92	2.78	5.44/2.52
I-IPH	1.08	-1.96	-1.86	2.94	2.86	5.44/2.50
II-TPH	1.11	-1.54	-1.37	2.48	2.71	5.47/2.99
II-IPH	1.12	-1.57	-1.39	2.51	2.81	5.48/2.97
I'-TPH	1.08	-	-	-	2.90	5.44/2.54
I'-IPH	1.09	-	-	-	3.00	5.45/2.45
II'-TPH	1.10	-	-1.41	2.51	2.79	5.46/2.95
II'-IPH	1.11	-	-1.52	2.63	2.87	5.47/2.84

^a Potential vs. Ag/AgCl in CH_3CN .

^b Potential vs. Ag/AgCl in DMF.

^c $E_{1/2}$ (Average potential of the redox couple peaks)

^d E_{g}^{EC} (Electrochemical band gap): Difference between E_{LUMO} and E_{HOMO} .

^e $E_{\text{g}}^{\text{opt}}$ (Optical band gap): Calculated from the polymer films ($E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$).

^f The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

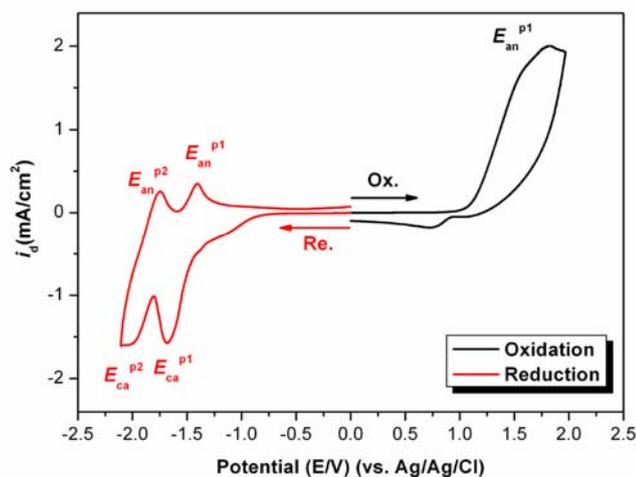


Figure 3. Cyclic voltammograms of the cast film of poly(1,3,4-oxadiazole) **II-TPH** on an ITO-glass substrate in MeCN (for the oxidation scan) and DMF (for the reduction scan) containing 0.1 M TBAP at a scan rate of 100 mV/s.

3.5 Spectro-electrochemical and electrochromic properties

For the spectroelectrochemistry investigations, typical result of the film of polyhydrazide **I-TPH** is presented in Figure 4 as a series of UV-vis absorbance curves correlated to electrode potentials. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 362 nm, characteristic for triarylamine, but it was pale yellow in the visible region. Upon oxidation of the **I-TPH** film (increasing applied voltage from 0 to 1.6 V), the intensity of the absorption peak at 362 nm gradually decreased while new peaks at 548 and 588 nm gradually increased in intensity, and the color of the film changed to dark green. We attribute this spectral change to the formation of a monocation radical of the pyrenylamine moiety.

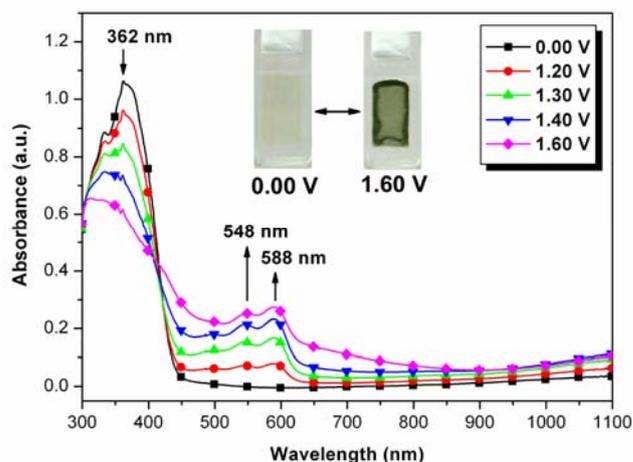


Figure 4. Spectral change of **I-TPH** thin film on the ITO-coated glass substrate (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage vs Ag/AgCl couple as reference. The inset shows the electrochromic photographic images of the film at indicated applied voltages.

4. Conclusions

A new family of electrochemically active polyhydrazides and poly(1,3,4-oxadiazole)s with diphenylpyrenylamine core have been synthesized. All the polymers could form morphologically stable and uniform amorphous films using solution-casting techniques. In addition to high T_g , high thermal stability and excellent fluorescent properties, the polymers also revealed electrochromic characteristics with color change from colorless or pale yellow neutral state to blackish green oxidized state. Thus, these high performance polymers may find optoelectronic applications as new hole-transporting, light-emitting, and electrochromic materials.

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