A New Class of High T_g and Organosoluble Aromatic Poly(amine−1,3,4-oxadiazole)s Containing Donor and Acceptor Moieties for Blue-Light-Emitting Materials

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Received January 27, 2006; Revised Manuscript Received July 9, 2006

ABSTRACT: A new naphthylamine-derived aromatic dicarboxylic acid, 1-[*N*,*N*-di(4-carboxyphenyl)amino]-naphthalene (**2**), was successfully synthesized by the sodium hydride-mediated condensation of 1-aminonaphthalene with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dicyano compound **1**. Four poly(amine−hydrazide)s were prepared from the polycondensation reactions of the dicarboxylic acid **2** and 4,4′-dicarboxytriphenylamine (**2′**) with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH), respectively, via the Yamazaki phosphorylation reaction. The poly(amine−hydrazide)s were readily soluble in many common organic solvents and could be solution cast into transparent and flexible films with good mechanical properties. These hydrazide polymers had glass-transition temperatures (T_g) in the range of 182−230 °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 had useful levels of thermal stability associated with high T_g (263−277 °C), 10% weight-loss temperatures in excess of 500 °C, and char yield at 800 °C in nitrogen higher than 54%. These polymers exhibited maximum UV−vis absorption at 344−391 and 352−391 nm in NMP solution and solid-state films, respectively. Their photoluminescence spectra in NMP solution showed maximum bands around 495−529 and 457−476 nm in the green and blue region for **TPH** and **IPH** series, respectively. The poly(amine−hydrazide) **(I-IPH)** derived from diacid **2** and IPH showed a blue photoluminescence at 457 nm with full-width at half-maximum (fwhm) of 85 nm and exhibited a 34% quantum yield in NMP solution. Blue electroluminescence characteristics were observed from the poly(amine−1,3,4-oxadiazole)s of **III-IPH** and **III-TPH**. Cyclic voltammograms of the poly(amine−hydrazide) films cast onto an indium−tin oxide (ITO)-coated glass substrate exhibited one oxidation redox couples (E_{onset}) at 1.11 V vs Ag/AgCl in dry acetonitrile solution, and revealed electrochromic characteristics with a color change from colorless to green at applied potentials switched between 0 and 1.6 V. The present study suggests that novel poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s have a great potential as new blue-emitting materials with hole-transporting and electrochromic characteristics.

Introduction

Since the first report of polymeric light-emitting diodes (LED) based on poly(*p*-phenylenevinylene)[1] triggered a large amount of interest in polymer emitting layers.[2] The advantages of the emitting polymeric materials over their molecular counterparts, first reported in 1987 by Tang and VanSlyke,[3] are an easy process for formation of films by spin-coating and drastic decrease in the potential for crystallization of the film which is quite common among small organic molecules. Organic light emitting diodes (OLEDs) are readily available in all three primary colors. However, blue-light-emitting materials remain an area of intense research activity to compete with the GaN-based inorganic LEDs. Furthermore, in full-color displays, the polymer with a large energy band gap that can efficiently emit blue light and also serve as the energy-transfer donor in the presence of low energy fluorophores is highly desirable. The polymers approach to blue electroluminescent devices are generally categorized into fully conjugated polymers and partially conjugated polymers with isolated chromophores which were attached in the main chain or side chain of polymers. However, the solubility of many highly conjugated polymers is low, particularly for blue-emitting species. These targeted blue-emitting polymers therefore often bear large alkyl, alkoxy, or aryloxy groups to improve solubility and thus lower their glass transition temperatures (T_gs) and thermal stability. Among these materials, conjugated polymers with donor−acceptor architectures are inspiring because the electron or hole affinities can be enhanced.[4]

Many blue-emitting polymers however have low quantum yield solid-state emission or sizable solid-state emission wavelength shifts relative to solution phase emission spectra, due to the presence of intramolecular charge transfer[5] and interchain interactions such as aggregation, excimer formation, and polaron pair formation.[6] There are some effective approaches to minimize these undesirable effects. For example, the isolated copoly(aryl ether)s consisting of defined hole-transporting (donor) or electron-transporting (acceptor) segments did enhanced electron and hole affinities simultaneously, among which the nonconjugated spacers conduced toward large band gap for

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10.1021/ma060205d CCC: $33.50

blue emission.[7] The introduction of an asymmetric meta-linkage in the main conjugated chain of the polymer also can limit interchain interaction as well as constrain exciton migration to quenching site.[8] The greater the torsion angle, the more interrupted the effective conjugated length or reduced interchain interaction. Another approach is to use bulky substituents to limit close packing between aromatic chromophores in the solid state.[9] In all these devices, for achieving efficient performance, tedious and complex multilayer structures were needed to offset the poor hole injection or electron affinity of the blue-light-emitting polymers. Therefore, it is desirable to design and synthesize a bipolar polymer that possesses both a hole-transporting segment and an electron-affinitive moiety to balance the rates of injection of holes and electrons.[10,11]

Oxadiazole derivatives are often associated with blue luminescent polymers as an electron transporting molecules either in the same layer or in a bilayer. Triarylamines also have attracted considerable interest as hole transport materials for use in multilayer organic electroluminescence (EL) devices due to their relatively high mobility and their low ionization potentials.[12] The feasibility of utilizing spin-coating and ink-jet printing processes for large-area EL devices and the possibilities for various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive.[13] To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives involving hole-transporting units such as triarylamine or carbazole group in the emissive π-conjugated core/main chains[14] or grafting them as side chains in a polymer[15] or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges.[16]

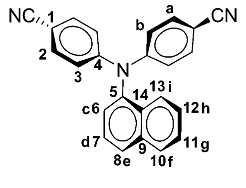
Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.[17,18] Recently, 1,3,4-oxadiazole-containing conjugated polymers have been widely investigated and applied as electron transport or emission layers in polymer light-emitting diodes (LEDs).[19,20] The primary reason for this use is the high photoluminescent quantum yield in the visible region that characterizes many of these materials, combined with the advantage of simple processability into flexible, mechanically robust films or thin layers. Unfortunately, aromatic polyoxadiazoles are difficult to process owing to their infusible and insoluble properties and their tendency to be brittle. To overcome these limitations, polymer-structure modification becomes necessary. Recently, we have reported the synthesis of soluble aromatic polyimides and polyamides bearing triphenylamine units in the main chain.[21] Because of the incorporation of bulky, propeller-shaped triphenylamine units along the polymer backbone, all the polymers were amorphous, showed good solubility in many organic solvents and good film-forming capability, and exhibited high thermal stability.

In this article, we therefore synthesized the novel naphthylamine-based dicarboxylic acid monomer, 1-[*N,N*-di(4-carboxyphenyl)amino]naphthalene, and the properties of its derived poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s will be investigated. The general properties such as solubility, film quality, and thermal properties are reported. The polymers synthesized are expected to exhibit outstanding thermal stability because of their wholly aromatic structure. In addition, the incorporation of 1-naphthyldiphenylamine units as functional parts along the polymer backbone is expected to enhance their solubility. The electrochemical, electrochromic, and luminescent properties of these polymers are also described herein and are compared with those of structurally related ones from 4,4′-dicarboxytriphenylamine.[22]

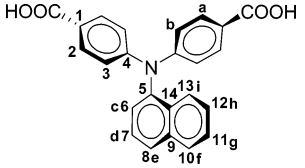
Experimental Section

Materials. 4,4′-Dicarboxytriphenylamine (mp: 313−315 °C) was synthesized by the cesium fluoride-mediated condensation of aniline with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dinitrile compound according to a previously reported procedure.[21b,22] 1-Aminonaphthalene (Tokyo Chemical Industries), 4-fluorobenzonitrile (TCI), sodium hydride (95%; dry)(Aldrich), potassium hydroxide (TEDIA), *N,N*-dimethylacetamide (DMAc) (TEDIA), *N,N*-dimethylformamide (DMF) (TEDIA), dimethyl sulfoxide (DMSO) (TEDIA), diphenyl phosphite (DPP) (ACROS), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), pyridine (Py) (TEDIA), *m*-cresol (ACROS) were used as received. Terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH) were purchased from TCI and used without further purification. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice from ethyl acetate and then dried in vacuo prior to use. All other reagents were used as received from commercial sources.

Monomer Synthesis. 1-[*N,N*-Di(4-cyanophenyl)amino]naphthalene (1). A mixture of 5.35 g (0.212 mol) of sodium hydride and 220 mL of DMF was stirred at room temperature for 30 min. To the mixture were added 15.55 g (0.103 mol) of 1-aminonaphthalene and 25.76 g (0.211 mol) of 4-fluorobenzonitrile in sequence. The mixture was heated with stirring at 170 °C for 15 h under nitrogen and then precipitated into 1800 mL of water/methanol (1:1). The product was filtered and recrystallized from acetic acid/water to afford 18.28 g (51% in yield) of light brown crystals with a mp of 170−171 °C. IR (KBr): 2222 cm^{-1} (C≡N stretch). ^1H NMR (DMSO-d_6, δ, ppm): 7.08 (d, 4H, H_b), 7.44−7.50 (m, 2H, $H_d + H_c$), 7.54 (t, 1H, H_h), 7.62 (t, 1H, H_g), 7.66 (d, 4H, H_a), 7.71 (d, 1H, H_e), 8.02−8.06 (m, 2H, $H_f + H_i$). ^{13}C NMR (DMSO-d_6, δ, ppm): 104.3 (C^1), 119.1 (CN), 121.4 (C^3), 122.7 (C^8), 127.0 ($C^{11} + C^{12}$), 127.8 (C^7), 128.4 (C^6), 128.8 (C^{13}), 129.1 (C^{10}), 130.3 (C^{14}), 134.0 (C^2), 135.2 (C^9), 140.2 (C^5), 150.0 (C^4). Anal. Calcd for $C_{24}H_{15}N_3$ (345.40): C, 83.46; H, 4.38; N, 12.17. Found: C, 83.32; H, 4.52; N, 12.35.



1-[*N,N*-Di(4-carboxyphenyl)amino]naphthalene (2). A mixture of 16.38 g (0.292 mol) of potassium hydroxide and 7.11 g (0.021 mol) of the obtained dinitrile compound **1** in 10 mL of ethanol and 35 mL of distillated water was stirred at approximately 100 °C until no further ammonia was generated. The time taken to reach this stage was about 4 days. The solution was cooled, and the pH value was adjusted by dilute hydrochloric acid to near 3. The white precipitate formed was collected by filtration, washed thoroughly with water and recrystallization from acetic acid/water, and dried in vacuo at 80 °C to give 6.41 g (81% in yield) of pale yellow crystals with a mp of 316−318 °C (by DSC). IR (KBr): 1686 (C=O stretch), 2700−3400 cm^{-1} (O−H stretch). ^1H NMR (DMSO-d_6, δ, ppm): 7.03 (d, 4H, H_b), 7.42 (t, 1H, H_h), 7.43 (d, 1H, H_c), 7.50 (t, 1H, H_g), 7.58 (t, 1H, H_d), 7.75 (d, 1H, H_i), 7.83 (d, 4H, H_a), 7.96 (d, 1H, H_e), 8.01 (d, 1H, H_f), 12.66 (s, 2H, OH). ^{13}C NMR (DMSO-d_6, δ, ppm): 120.5 (C^3), 122.9 (C^{13}), 124.2 (C^1), 126.6 (C^{11}), 126.8 (C^7), 127.3 (C^{12}), 127.9 (C^6), 128.0 (C^{10}), 128.8 (C^8), 130.4 (C^{14}), 131.0 (C^2), 135.0 (C^9), 141.2 (C^5), 150.5 (C^4), 166.9 (C=O). Anal. Calcd for $C_{24}H_{17}NO_4$ (383.40): C, 75.19; H, 4.47; N, 3.65. Found: C, 75.19; H, 4.30; N, 3.67.



Polymer Synthesis. The poly(amine−hydrazide)s were synthesized from dicarboxylic acid monomer **2** and dihydrazides, TPH and IPH, via phosphorylation polycondensation method. A typical synthetic procedure for poly(amine−hydrazide) **I-IPH** is described as follows. A dried 50 mL flask was charged with **2** (0.383 g; 1 mmol), IPH (0.194 g; 1 mmol), NMP (1 mL), calcium chloride (0.12 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 as quantitative, and the inherent viscosity of the poly(amine−hydrazide) **I-IPH** was 0.26 dL/g, measured in NMP at a concentration of 0.5 g/dL at 30 ?. IR (film): 3272 (N−H), 1656 cm^{-1} (C═O). The other poly(amine−hydrazide)s were prepared by an analogous procedure.

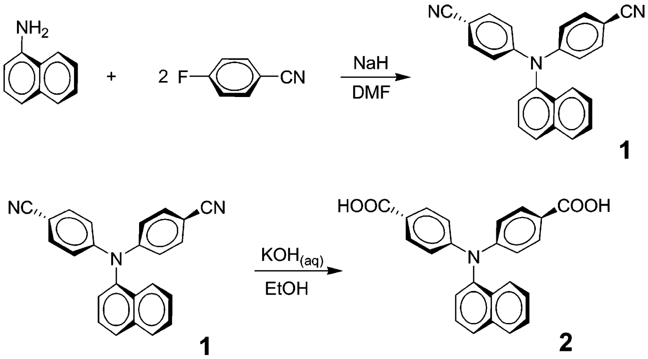
Poly[2,7-(9,9-dihexylfluorene)] (PF). First, 502 mg of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (1 mmol), 492 mg of 9,9-dihexyl-2,7-dibromofluorene (1 mmol), and 10 mL of toluene were used to afford 600 mg of light yellow solid (90.3%). ^1H NMR ($CDCl_3$), δ (ppm): 0.80 (br, 10H), 1.15 (br, 12H), 2.15 (br, 4H), 7.68−7.86 (m, br, 6H). 13C NMR (CDCl3), δ (ppm): 14.02, 22.56, 23.85, 29.67, 31.46, 40.36, 55.33, 119.98, 121.52, 126.15, 140.02, 140.53, 151.81. Anal. Calcd for $C_{25}H_{32}$ (%): C, 90.30; H, 9.70. Found: C, 89.76; H, 9.60.

Film Preparation and Cyclodehydration of the Hydrazide Polymers. A solution of polymer was made by dissolving about 0.7 g of the poly(amine−hydrazide) **I-IPH** sample in 8 mL of DMAc, and the homogeneous solution was poured into a 9 cm glass culture dish, which was heated at 50 °C for 1 h, 100 °C for 2 h, and 160 °C for 5 h to slowly release the solvent under vacuum. The obtained film with the thickness of 30−40 μm was used for X-ray diffraction measurements, solubility tests, thermal analyses, optical and electrochemical properties, and electrochromic characteristics measurements.

The cyclodehydration of the poly(amine−hydrazide) **I-IPH** to the corresponding poly(amine−1,3,4-oxadiazole) **III-IPH** was carried out by successive heating the above fabricated polymer films at 200 °C for 30 min, 300 °C for 1 h, and then 350 °C for 3 h under vacuum. Anal. Calcd for $(C_{32}H_{19}N_5O_2)_n$ $(505.53)_n$: C, 76.03; H, 3.79; N, 13.85. Found: C, 75.83; H, 3.72; N, 13.78.

Measurements. Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. Elemental analyses were run in Elementar VarioEL-III. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV-500 FT-NMR system. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-7000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu−Kα radiation. Ultraviolet−visible (UV−vis) spectra of the polymer films were recorded on a Varian Cary 50 Probe spectrometer. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6−8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm^3/min). Cyclic voltammetry was performed with a Bioanalytical System model CV-27 potentiostat and a BAS X−Y recorder with ITO (polymer films area about 0.7 cm × 0.5 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in solution of 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH_3CN). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (saturated) reference electrode. The spectroelectrochemical cell 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 spectroelectochemical analysis were measured with a HP 8453 UV−visible spectrophotometer. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer. Fluorescence quantum yields (Φ_F) of the samples in NMP were measured by using quinine sulfate in 1 N H_2SO_4 as a reference standard ($\Phi_F = 0.546$)[23] were used. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra.

Scheme 1. Monomer Synthesis



Device Fabrication and Testing. The electroluminescent (EL) devices were fabricated on indium−tin oxide (ITO) coated glass substrate with sheet resistance of 20−30 Ω/sq. The substrate was ultrasonically cleaned with detergent, deionized water, acetone, and methanol, subsequently. Onto the ITO glass a layer of poly(ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT: PSS), 50−60 nm thick (probed by Alpha-Step 500 Surface Profiler), was formed by spin-coated from its aqueous solution (Baytron P 8000, Bayer). The single-layer emissive layer was spin-coated at 3000 rpm from the **IPH** (or **TPH**) in NMP solution (1.5 wt %) on top of the vacuum-dried PEDOT:PSS layer and dried in a vacuum at 150 °C for 15 min. In the following, under a base pressure below 2×10^4 Torr, a layer of Ca (10 nm) was vacuum deposited as cathode and a thick layer of Ag (100 nm) was deposited subsequently as the protecting layer. The cathode area defines the active area of the

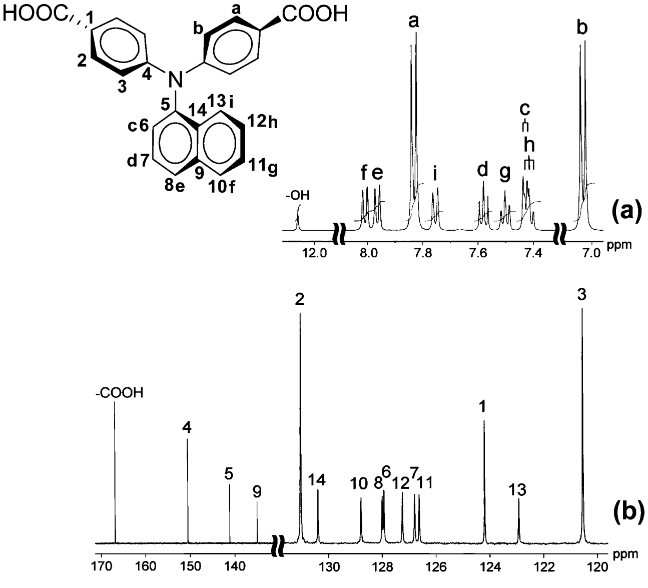


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of compound **2** in DMSO-d_6.

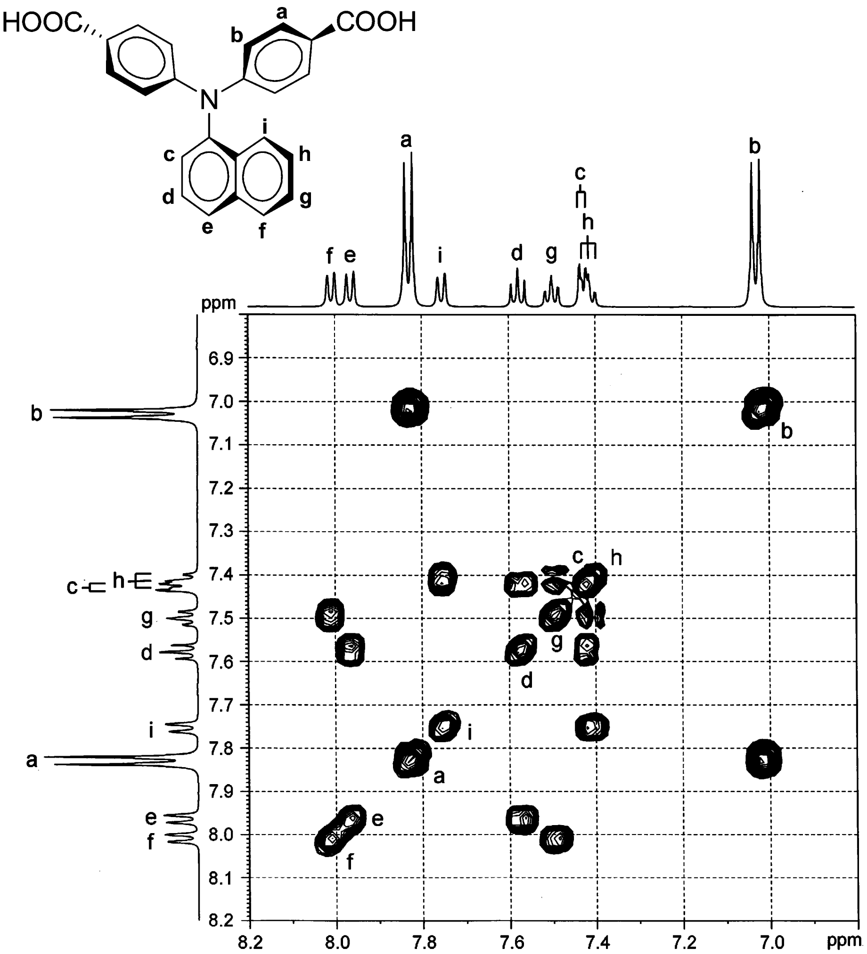
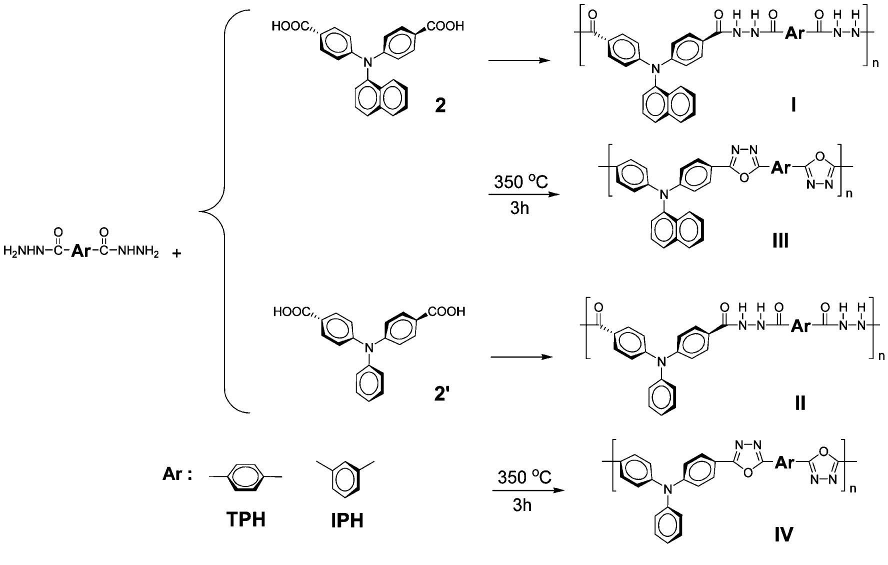


Figure 2. H−H COSY spectrum of diacid **2** in DMSO-d_6.

Scheme 2. Synthesis of Poly(amine−hydrazide)s and Poly(amine−1,3,4-oxadiazole)s



device, which is 0.1256 cm^2 in this study. Current−voltage characteristics were measured with a computerized Keithley 2400 source measure unit. The luminance and CIE coordinate of device were measured with a Konica-Minolta Chroma Meter CS-100A. The EL spectrum of device was recorded on a Fluorolog-3 spectrofluorometer (Jobin Yvon).

Results and Discussion

Monomer Synthesis. The new aromatic dicarboxylic acid having a bulky pendent naphthylamine group, 1-[*N*,*N*-di(4-carboxyphenyl)amino]naphthalene (**2**), was successfully synthesized by the condensation reaction of 1-aminonaphthalene with 4-fluorobenzonitrile in DMF in the presence of sodium hydride as a base, followed by the alkaline hydrolysis of the intermediate dinitrile compound, according to the synthetic route outlined in Scheme 1. Elemental analysis, IR, and ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify structures of the intermediate dinitrile compound **1** and dicarboxylic acid monomer **2**. Figure 1 illustrates the ^{1}H NMR and ^{13}C NMR

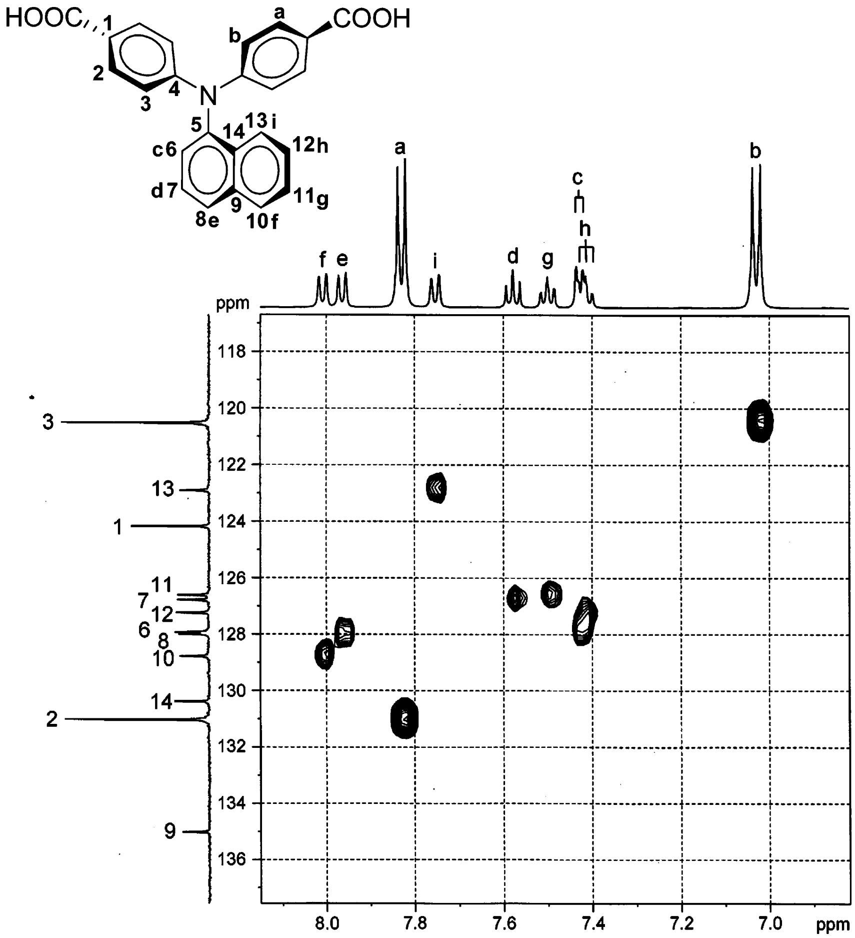


Figure 3. C−H HMQC spectrum of diacid **2** in DMSO-d_6.

spectra of the dicarboxylic acid monomer **2**. Assignments of each carbon and proton are assisted by the two-dimensional NMR spectra shown in Figures 2 and 3, and these spectra agree well with the proposed molecular structure of monomer **2**.

Polymer Synthesis. A two-step procedure was employed to obtain the poly(amine−1,3,4-oxadiazole)s from the newly synthesized dicarboxylic acid monomer **2** and 4,4′-dicarboxytriphenylamine (**2′**) with TPH and IPH (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 fiberlike form when slowly pouring the resulting polymer solutions into methanol. The obtained poly(amine−hydrazide)s had inherent viscosities in the range of 0.26−0.37 dL/g (Table 1).

Table 1. Inherent Viscosity[a] and Solubility[b] of Poly(amine−hydrazide)s and Poly(amine−1,3,4-oxadiazole)s

polymer			Solvent						
Code	η_{inh} (dL/g)	Color of film[c]	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Chloroform
I-TPH	0.37		+ +	+ +	+ +	+ +	+	-	-
I-IPH	0.26		+ +	+ +	+ +	+ +	+	-	-
II-TPH	0.56		+ +	+ +	+ +	+ +	+	-	-
II-IPH	0.61		+ +	+ +	+ +	+ +	+	-	-
III-TPH	0.32		+ +	+	+	+	+	-	-
III-IPH	0.22		+ +	+	+	+	+	-	-
IV-TPH	-		+ -	-	-	-	-	-	-
IV-IPH	-		+ -	-	-	-	-	-	-

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C. (**III-TPH** and **III−IPH** measured in concentrated sulfuric acid). [b] Solubility: ++, soluble at room temperature; +, soluble on heating; +−, partially soluble or swelling; −, insoluble even on heating. [c] The photographs are the appearance of the polymer films (thickness = 1−3 μm).

Thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring was confirmed with elemental analysis and IR spectroscopy. As a representative study, a thin-film sample of polyhydrazide **I-TPH** was heated at 350 °C for 3 h. The IR spectra of these polymers exhibited the disappearance of the absorption at 3272 (N−H), 1656 cm^{-1} (C=O), and the characteristic 1,3,4-oxadiazole ring vibration at around 1500−1600 (C=N) and 1071 cm^{-1} (C−O−C). DSC also could be used to investigate cyclization to the oxadiazole structure. A typical pair of DSC curves of poly(amine−hydrazide), **I-TPH**, and poly(amine−1,3,4-oxadiazole), **III-TPH**, are illustrated in Figure 4. The main endothermic peak revealed the cyclodehydration reaction of hydrazide group with water evolution in the range of 300−400 °C. The heat-converted poly(amine−1,3,4-oxadiazole)s had inherent viscosities in the range of 0.22−0.32 dL/g.

Polymer Solubility and Film Morphology. The solubility behavior of all the polymers and the appearance of the cast films are shown in Table 1. These low-colored polymers exhibited

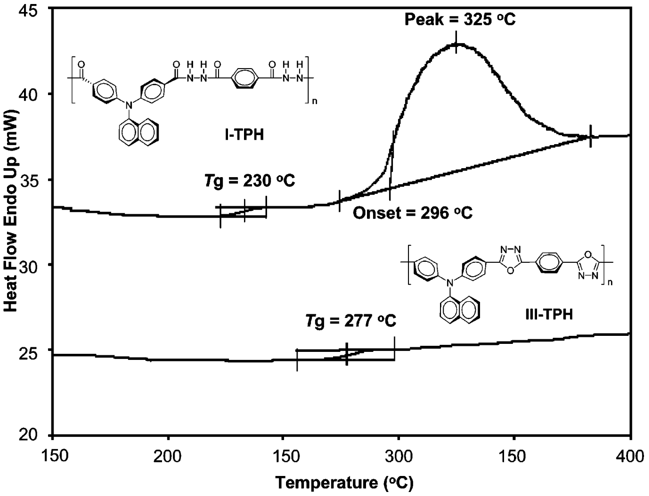


Figure 4. DSC traces of (a) poly(amine−hydrazide) **I-TPH** and (b) poly(amine−1,3,4-oxadiazole) **III-TPH** with a heating rate of 20 °C/min in nitrogen.

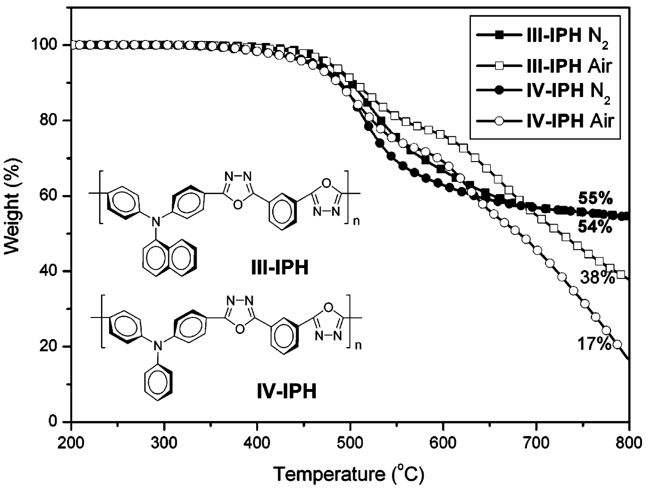


Figure 5. TGA thermograms of poly(amine−1,3,4-oxadiazole)s **III-IPH** and **III-IPH** at a scan rate of 20 °C/min.

good solubility in variety solvents such as NMP, DMAc, DMF, DMSO and *m*-cresol. Compared with triphenylamine-based poly(amine−1,3,4-oxadiazole)s **IV** series, the enhanced solubility of the **III** series can be attributed to the introduction of the bulky, asymmetric, and noncoplanar 1-naphthyldiphenylamine group into the repeat unit, which interrupts the chain packing and decreases the interchain interactions. Thus, the excellent solubility makes these polymers as potential candidates for practical applications by spin-coating or ink-jet printing processes.

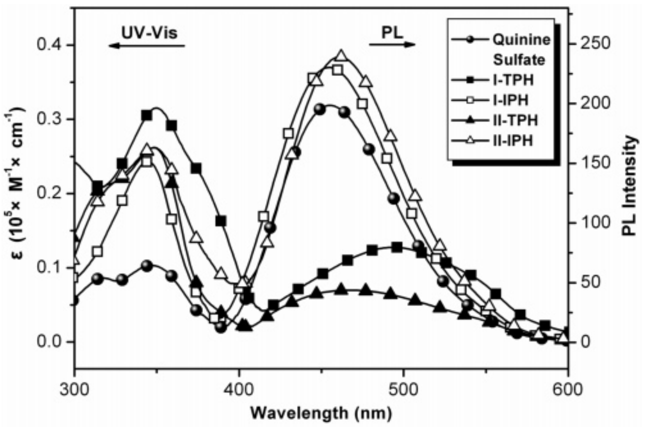


Figure 6. UV−vis absorptions and PL spectra of poly(amine−hydrazide)s in NMP solution (10^{-5} M). Quinine sulfate dissolved in 1 N H_2SO_4(aq) (10^{-5} M) as the standard. ($\Phi_F = 0.546$.)

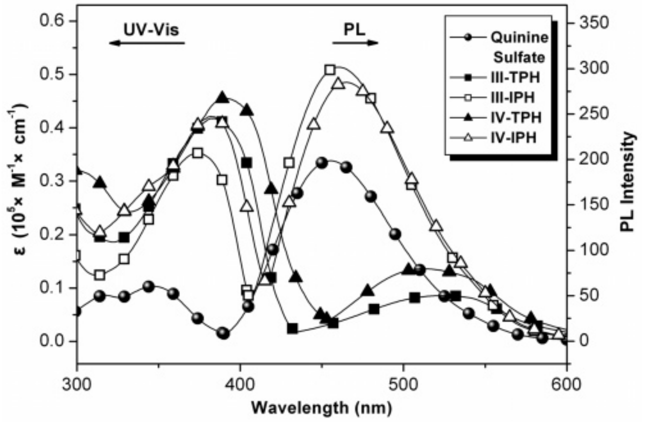


Figure 7. UV−vis absorptions and PL spectra of poly(amine−1,3,4-oxadiazole)s in NMP solution (10^{-5} M). Quinine sulfate dissolved in 1 N H_2SO_4(aq) (10^{-5} M) as the standard. ($\Phi_F = 0.546$.)

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 amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional 1-naphthyldiphenylamine unit along the polymer backbone.

Thermal Properties. The thermal properties of poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s are summarized in Table 2. The glass-transition temperatures (T_g) of poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s were observed in the range of 182−230 and 263−277 °C by DSC. Typical TGA curves for poly(amine−1,3,4-oxadiazole) **III-TPH** and **IV-TPH** are reproduced in Figure 5. All of the poly(amine−1,3,4-oxadiazole)s exhibited a similar TGA pattern with no significant weight loss below 500 °C in air or nitrogen atmosphere. The 10% weight-loss temperatures (T_d^{10}) of the poly(amine−1,3,4-oxadiazole)s in nitrogen and air were

Table 2. Thermal Behavior of Poly(amine−hydrazide)s[a] and Poly(amine−1,3,4-oxadiazole)s[b]

poly(amine−hydrazide)				poly(amine−1,3,4-oxadiazole)							
						T_d^5 (°C)[d]		T_d^{10} (°C)[e]		char yield(wt %)[f]	
code	T_g (°C)	T_o (°C)	T_p (°C)	code	T_g (°C)[c]	N_2	air	N_2	air	N_2	air
I-TPH	230	296	325	**III-TPH**	277	475	485	505	515	58	25
I-IPH	218	302	334	**III-IPH**	263	480	480	505	505	55	38
II-TPH	197	300	326	**IV-TPH**	264	445	455	490	490	61	40
II-IPH	182	303	342	**IV-IPH**	263	460	455	490	485	54	17

[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 h prior to all the thermal analyses. [c] Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C/min) of the sample after quenching from 400 to 50 °C (rate: 200 °C/min) in nitrogen. [d] Temperature at which 5% weight loss occurred, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 cm^3/min. [e] Temperature at which 10% weight loss occurred. [f] Residual weight percentage when heated to 800 °C.

Table 3. Optical and Electrochemical Properties for Poly(amine−hydrazide)s and Poly(amine−1,3,4-oxadiazole)s

	solution λ (nm)^a			film λ (nm)					reduction^k (V)						
									$E_{1/2}$^{f}						
index	abs max	PL max^b	Φ_F (%)^c	λ_0^{d}	abs max	abs onset	PL max^b	oxidation^j (V) E_{onset}	first	second	E_{onset}	E_g^{EC} (eV)^h	E_g^{opt} (eV)^i	HOMO^g (eV)	LUMO (eV)
I-TPH	350	494	13	422	352	398	475	1.11	*e*				3.08	5.47	2.39
I−IPH	344	455	34	401	352	399	451	1.11					3.11	5.47	2.36
II-TPH	348	467	8	408	359	406	475	1.08					2.97	5.44	2.47
II−IPH	349	461	33	405	357	405	457	1.08					2.99	5.44	2.45
III-TPH	382	527	5	437	382	439	482	1.12	−1.56	−1.90	−1.49	2.61	2.83	5.48	2.87
III-IPH	374	463	32	420	381	423	466	1.12	−1.69	−1.99	−1.60	2.72	2.93	5.48	2.76
IV-TPH	391	515	7	440	391	450	494	1.09	−1.51	−1.80	−1.41	2.50	2.75	5.45	2.95
IV-IPH	381	468	24	427	381	434	466	1.09	−1.64	−1.86	−1.55	2.64	2.86	5.45	2.71

[a] Polymer concentration of 10^{-5} mol/L in NMP. [b] They were excited at abs_{max} for both solid and solution states. [c] The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard ($\Phi_F = 0.546$). [d] The cutoff wavelength from the UV−vis transmission spectra of polymer films. (thickness: 1−3 μm) [e] No discernible oxidation redox was observed. [f] $E_{1/2}$ (average potential of the redox couple peaks). [g] The HOMO and LUMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). [h] E_g^{EC}: Electrochemical band gap is derived from the difference between the LUMO and HOMO levels. [i] E_g^{opt}: Optical band gap is derived from polymer films ($E_g = 1240/\lambda_{onset}$). [j] vs Ag/AgCl in CH_3CN(aq). [k] vs Ag/AgCl in DMF(aq).

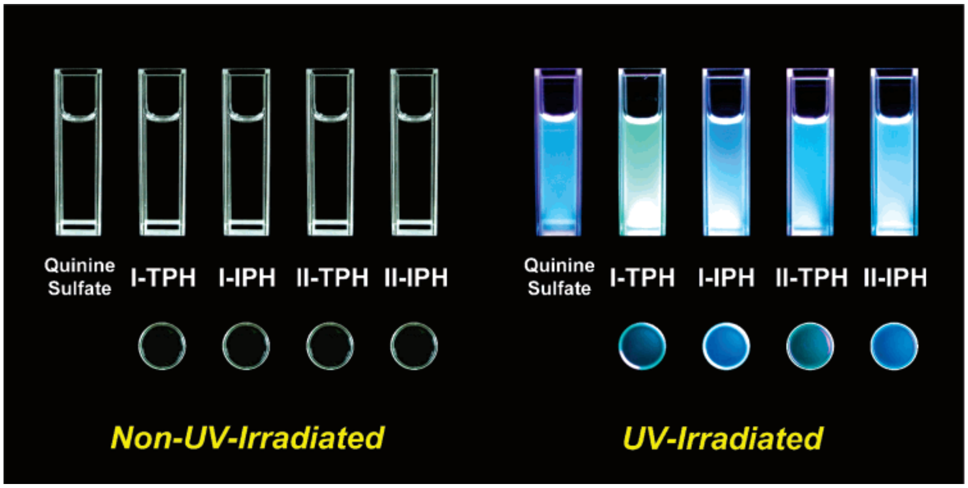


Figure 8. Photoluminescence of poly(amine−hydrazide) solutions (10^{-5} M) and thin films (thickness: 1−3 μm) by UV irradiation (excited at 365 nm). Quinine sulfate dissolved in 1 N H_2SO_4(aq) (10^{-5} M) as the standard. ($\Phi_F = 0.546$.)

recorded in the ranges 501−590 and 495−515 °C, respectively. The amount of carbonized residue (char yield) of these polymers was more than 55% at 800 °C in nitrogen. The high char yields of these polymers can be ascribed to their high aromatic content. As shown in Table 2, when compared with the analogous poly(amine−1,3,4-oxadiazole)s **IV**, the **III** series showed an increased T_g and an enhanced thermal stability (Figure 5) because of the introduction of planar naphthalene groups in the repeat unit.

Optical Properties. The optical properties of the poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s were investigated by UV−vis and photoluminescence (PL) spectroscopy. The results are summarized in Table 3. These soluble polymers **I**−**IV** exhibited maximum UV−vis absorption bands at 344−391 nm in NMP solution, assignable to the $\pi-\pi^*$ transition resulting from the conjugation between the aromatic rings and nitrogen atoms that combines the characteristic $\pi-\pi^*$ transitions of naphthalene chromophore (350 nm).[24] The UV−vis absorptions of naphthylamine-based poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s in film state showed single absorbance at 352−359 and 381−391 nm. Figures 6 and 7 show UV−vis absorption and photoluminescence spectra of poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s in NMP solutions (10^{-5} mol/L). The 1-naphthyldiphenylamine-containing poly(amine−hydrazide) **I-IPH** and poly(amine−1,3,4-oxadiazole) **III-IPH** exhibited blue fluorescence emission maxima at 455 and 463 nm in NMP solution with quantum yields of 34% and 32%. Compared with **II-IPH** and **IV-IPH**, the higher fluorescence quantum yield of **I-IPH** and **III-IPH** could be attributed to the incorporation of naphthalene chromophore. The photoluminescence of poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s in solution and film state under UV irradiation are shown in Figures 8 and 9. The absorption and photoluminescence spectra of the polymers in film states have been provided below as Figure S1. **I-TPH** and **III-TPH** in Table 3 reveal large blue shift of maximum PL peak from solution to film state, which could be attributed to the solvent effect that was found for the triphenylamine-containing polymer system in our lab, and exhibited more red shift with increasing solvent polarity and symmetry (Figure S2). It is characteristic of donor−acceptor containing polymer similar to that reported in ref 26b. The cutoff wavelengths (absorption edge; λ_0) from the UV−vis transmittance spectra showed light-color and high optical transparency with cutoff wavelength in the range of 401−440 nm.

Electrochemical Properties. The electrochemical properties of the poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s were investigated by cyclic voltammetry. The results are summarized in Table 3. The redox behavior of these polymers was investigated by cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) and *N*,*N*-dimethylformamide (DMF)

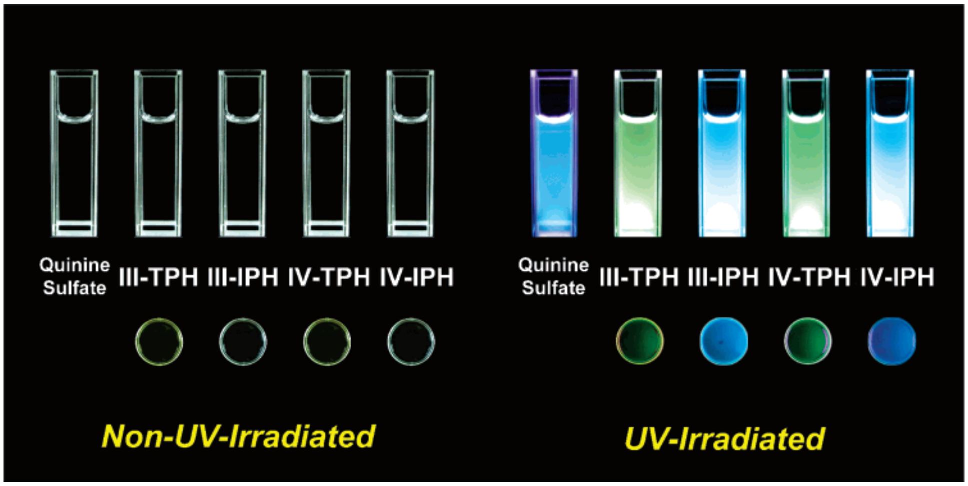


Figure 9. Photoluminescence of poly(amine−1,3,4-oxadiazole) solutions (10^{-5} M) and thin films (thickness: 1−3 μm) by UV irradiation (Excited at 365 nm). Quinine sulfate dissolved in 1 N H_2SO_4(aq) (10^{-5} M) as the standard. ($\Phi_F = 0.546$.)

Table 4. Electroluminescence Characteristics Based on the Device Structures of ITO/PEDOT:PSS/Emissive Layer/Ca/Ag

	emission maximum (nm)	bias (V)	CIE (x, y)[a]	V_t (V)[b]	brightness (cd/m^2)	luminance yield (cd/A)
III-IPH	451	11	(0.245, 0.319)	5	18.4	0.0055
III-TPH	469	9.5	(0.232, 0.297)	5	17.9	0.0045
PF	422, 447, 476	11	(0.221, 0.264)	6.5	103	0.188

[a] The commission Internationale de L'Eclairage (CIE) 1931 coordinates. [b] Threshold voltage.

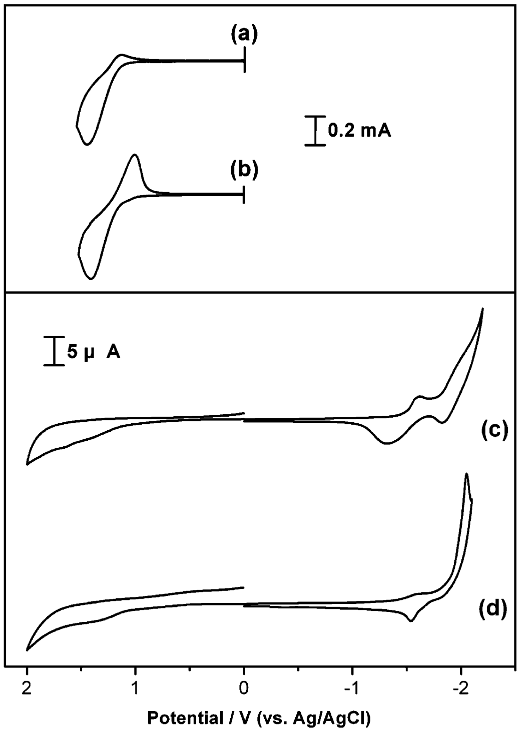


Figure 10. Cyclic voltammograms of poly(amine−hydrazide) (a) **I-TPH** and (b) **II-TPH** and poly(amine−1,3,4-oxadiazole) (c) **III-TPH** and (d) **IV-TPH** films onto an indium−tin oxide (ITO) coated glass substrate in CH_3CN (oxidation) and DMF (reduction) solution containing 0.1 M TBAP at scan rate = 0.1 V/s.

containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere for oxidation and reduction measurements. Figure 10 shows the typical cyclic voltammograms for poly(amine−hydrazide)s **I-TPH** and **II-TPH** and poly(amine−1,3,4-oxadiazole)s **III-TPH** and **IV-TPH**. The poly(amine−hydrazide)s **I-TPH** and **II-TPH** undergo one oxidation processes at E_{onset} = 1.11 and 1.08 V, and the oxidation and reduction onset potentials of poly(amine−1,3,4-oxadiazole)s **III-TPH** and **IV-TPH** are observed at +1.12 and +1.09 V and −1.49 and −1.41 V, respectively.[25] Comparing the electrochemical data, it was found that poly(amine−hydrazide) **II-TPH** is slightly easier oxidized than poly(amine−hydrazide) **I-TPH** (1.08 vs 1.11 V) due to the fact that the naphthalene ring is more stable than benzene in conjugation. In addition, the oxidation potentials of poly(amine−hydrazide)s were almost the same as the corresponding poly(amine−1,3,4-oxadiazole)s that also could explain these polymers with donor acceptor moieties are isolated system. The energy of the HOMO and LUMO levels of the corresponding polymers can be determined from the oxidation onset, reduction onset potentials (E_{onset}) and the onset absorption wavelength of the UV−vis irradiation, and the results are listed in Table 3. For example (Figure 10), the oxidation onset for poly(amine−hydrazide) **I-TPH** has been determined as 1.11 V vs Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard $E_{1/2}$ is 0.44 V vs Ag/AgCl in CH_3CN. Assuming that the HOMO energy for the Fc/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 5.47 eV. Thus, the HOMO and LUMO energies for poly(amine−1,3,4-oxadiazole) **III-TPH** could be evaluated to be 5.48 and 2.87 eV, respectively.

Device Fabrication and Electroluminescence Properties. The electroluminescence (EL) spectra of **III-IPH**, **III-TPH**, and **PF** based devices shown in Figure 11 have the emission maxima at 451, 469, and (415, 441, 471) nm, respectively. The EL characteristics are summarized in Table 4. The **III-IPH** and **III-TPH** show blue EL with the CIE coordinates of (0.245, 0.319) and (0.232, 0.297), respectively. However, the luminescence yield and brightness of the two polymers are lower than those of the **PF**,[26b] which is probably because of poor charge recombination resulted from the intramolecular charge transfer between the 1-naphthyldiphenylamine and oxidazole moieties. Similar donor−acceptor organic molecules also suggested

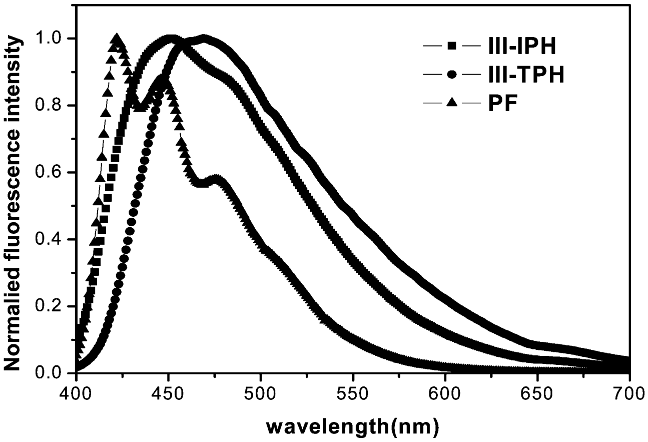


Figure 11. Electroluminescence spectra of **III-IPH**, **III-TPH**, and **PF** based on the device structures of ITO/PEDOT:PSS/emissive layer/Ca/Ag.

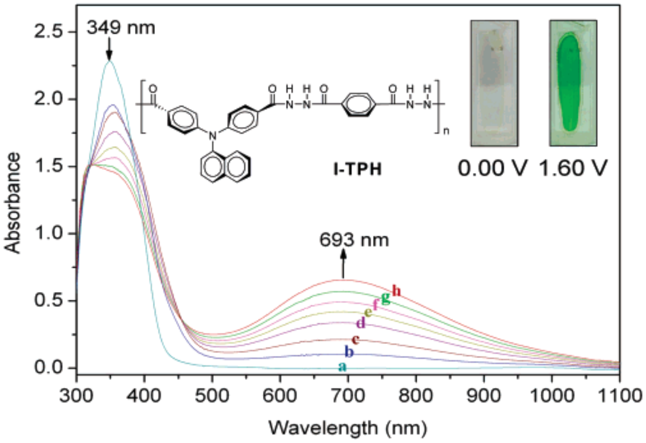


Figure 12. Electrochromic behavior of poly(amine−hydrazide) **I-TPH** thin film (in CH_3CN(aq) with 0.1 M TBAP as the supporting electrode) at (a) 0.00, (b) 1.00, (c) 1.10, (d) 1.20, (e) 1.30, (f) 1.40, (g) 1.50, (h) and 1.60 V.

similar EL characteristics.[26] Besides, the 1-naphthyldiphenylamine and oxidazole based polymers are more suitable to be used as the hole-transporting and electron-transporting materials, respectively, than the emissive materials in the present study.

Electrochromic Characteristics. Spectroelectrochemical analysis of the poly(amine-imide) films was carried out on an ITO-coated glass substrate, and they showed electrochromic behavior when the applied potential was changed. The color of the polymers was changed from neutral colorless to green. The typical spectroelectrochemical behavior of poly(amine−hydrazide) **I-TPH** at various applied potentials is depicted in Figure 12. When the applied potentials increased positively from 0.00 to 1.60 V, the peak of characteristic absorbance at 349 nm for poly(amine−hydrazide) **I-TPH** decreased gradually while one new band grew up at 693 nm due to the electron oxidation. The new spectrum was assigned as that of the stable cationic radical poly(amine−hydrazide)$^{+\bullet}$.[21] As the applied potential increased to the oxidation side, the film color changed from colorless to green (as shown in Figure 13). The stable cationic radical poly(amine−hydrazide)$^{+\bullet}$ was generated and exhibited strong bands as determined by UV−vis spectroelectrochemical methods.

Conclusions

The newly triarylamine-containing aromatic dicarboxylic acid, 1-[*N*,*N*-di(4-carboxyphenyl)amino]naphthalene (**2**) was successfully synthesized in high purity and good yields. Novel aromatic poly(amine−hydrazide)s were prepared from the dicarboxylic acid with terephthalic dihydrazide (TPH) and isophthalic dihydrazide (IPH), respectively, via the Yamazaki phosphorylation reaction, and were thermally cyclodehydrated into the corresponding poly(amine−1,3,4-oxadiazole)s. The introduction of the bulky naphthalene group into the polymer backbone disrupt the copolanarity of aromatic units in chain packing which increases the between-chains spaces or free volume thus enhancing solubility and thermal stability of the formed poly(amine−1,3,4-oxadiazole)s. All the polymers were amorphous with high optical transparency from UV−vis transmittance measurement with cutoff wavelength in the range of 401−437 nm. The poly(amine−hydrazide) **I-IPH** and poly(amine−1,3,4-oxadiazole)s **III-IPH** exhibited blue fluorescence emission maximum at 455 and 463 nm in NMP solution with high quantum yield of 34% and 32% due to the 1-naphthyldiphenylamine chromophore. All obtained poly(amine−hydrazide)s revealed good stability of electrochromic characteristics, changing color from the colorless neutral form to the green oxidized forms when scanning potentials positively from 0.00 to 1.60 V. Thus, our novel poly(amine−hydrazide)s and poly(amine−1,3,4-oxadiazole)s have a great potential as a new blue-emitting having hole-transporting characteristic and electrochromic materials due to their proper HOMO values, excellent thermal stability, solubility, quantum efficiency, and electrochemical behavior.

Acknowledgment. The authors are grateful to the National Science Council of the Republic of China for financial support of this work. The technical assistance on the electroluminescence measurement from Mr. Wen-Ya Lee of National Taiwan University is highly appreciated.

Supporting Information Available: Figures showing UV−vis absorption and photoluminescence spectra of polymer films **I-TPH** and **III-TPH** and UV−vis absorption and photoluminescence spectra of polymers, **I-TPH** and **III-TPH**, in NMP and THF solutions, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA060205D