Synthesis, Photophysical, and Electrochromic Characterization of Wholly Aromatic Polyamide Blue-Light-Emitting Materials

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ABSTRACT: A new carbazole-derived triphenylamine-containing aromatic dicarboxylic acid monomer, 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine, with blue light (460 nm) fluorescence quantum yield of 40% was successfully synthesized by the cesium-fluoride-mediated condensation of *N*-(4-aminophenyl)carbazole with 4-fluorobenzonitrile, followed by alkaline hydrolysis of the dinitrile intermediate. A series of novel poly(amine-amide)s with pendent *N*-phenylcarbazole units having inherent viscosities of 0.36−0.61 dL/g were prepared from the newly synthesized dicarboxylic acid monomer and various aromatic diamines by direct phosphorylation polycondensation. The obtained polymers were amorphous and could afford flexible, transparent, and tough films with good mechanical properties. They had useful levels of thermal stability associated with relatively high glass-transition temperatures (269−322 °C). These polymers exhibited strong UV−vis absorption maxima at 340−361 nm, and their photoluminescence showed emission peaks around 449−465 nm with quantum yields up to 46% in NMP solution. The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the poly(amine-amide) films prepared by casting polymer solution onto an indium−tin oxide (ITO)-coated glass substrate exhibited one reversible oxidative redox couples at potentials of 1.11−1.18 V vs Ag/AgCl in acetonitrile solution due to oxidation of main-chain triphenylamine unit. The polymer films revealed excellent stability of electrochromic characteristics for the radical cations generated, changing color from original yellowish to deep blue.

Introduction

Highly electron-rich and redox-active compounds are potentially useful building blocks in material science. Triarylamines 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.[1] The feasibility of utilizing spin-coating and ink-jet printing processes for large-area EL devices and possibilities of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive.[2] 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[3] or grafting them as side chains in a polymer[4] or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges.[5]

Carbazole is another well-known hole-transporting and electroluminescent unit. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, electroluminescent, and photorefractive materials.[6] From a structural point of view, carbazole differs from diphenylamine in its planar structure because it can be further imagined as the bonded diphenylamine; the thermal stability of materials with the incorporation of carbazolyl units therefore was improved. In addition, carbazole can be easily functionalized at the (3,6),[7,8] (2,7)[9] or *N* (or 9)-positions[10−12] and then covalently linked into polymeric systems, both in main chain[13] as building blocks and in side chain as pendent groups.[14] However, to the best of our knowledge, the literature dealing with the structures and properties of aromatic polyamides with chromophoric carbazole unit is nil. It is thus worthy to explore the feasibility of new carbazole-based aromatic diacid as a starting monomer for preparation of a high-performance polyamide system with novel optoelectronic functions. The introduction of these bulky pendent groups would interrupt the chain-chain hydrogen bonding of the polyamides and reduce chain-packing efficiency, which enhance solubility while maintaining high glass-transition temperatures (T_g) or softening temperatures (T_s) through decreased segmental mobility resulting from steric hindrance. In addition, the prepared carbazole-containing polyamides may find application in an organic electroluminescent element.

Wholly aromatic polyamides have been well-known for their excellent mechanical properties, high thermal stability, and good chemical resistance.[15] They are also known as difficult processing materials because of their high T_g or T_s and insoluble nature in most organic solvents. To overcome such a difficulty, polymer structure modification becomes necessary such as introduction of pendent groups (aromatic or alkyl groups) onto the polymer chains and incorporation of noncoplanar structural units in the main chains.[16] To achieve such a goal, much effort has been achieved in designing and synthesizing new diamines[17] and/or dicarboxylic acids,[18] which can fulfill this requirement, thus producing a great variety of soluble and processable polyamides for various purposes.

The electrochemistry of triphenylamine in aprotic solvents was well studied.[19] Triphenylamine cationic radical of the first electron oxidation is not stable; the chemical reaction therefore follow up to produce tetraphenylbenzidine by tail-to-tail (para-

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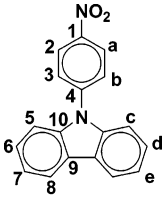
positions) coupling with the loss of two protons per dimer. When the phenyl groups were incorporated by electron-donating substitutents at the para-position of triarylamines, the coupling reactions were greatly prevented that afforded stable cationic radicals.[20,21] In this article, we therefore synthesized the novel carbazole-based diacid monomer, 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine **(4)**, and its derived poly(amine-amide)s containing electron-rich triphenylamine groups with carbazolyl para-substituted on the pendent phenyl ring. The general properties such as solubility, crystallinity, and thermal and mechanical properties are described. The electrochemical, electrochromic, and photoluminescent properties of these polymers prepared by casting solution onto an indium−tin oxide (ITO)-coated glass substrate are also described herein.

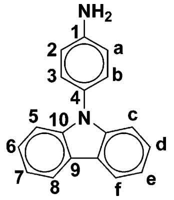
Experimental Section

Materials. *N*,*N*-Bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine,[17a] 2,2′-bis(4-aminophenoxy)biphenyl,[22] and 2,2′-bis(4-amino-2-trifluoromethyl- phenoxy)biphenyl[23] were synthesized according to reported methods. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 3 h. Tetrabutylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use. Solvents and other reagents were used as received from commercial suppliers.

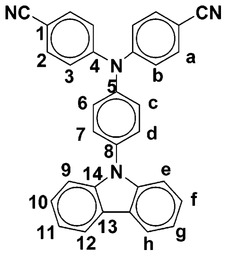
Monomer Synthesis. *N-(4-Nitrophenyl)carbazole (***1***)*. A mixture of 15.20 g (0.10 mol) of cesium fluoride in 70 mL of dimethyl sulfoxide (DMSO) was stirred at room temperature. To the mixture, 8.36 g (0.05 mol) of carbazole and 7.14 g (0.051 mol) of 4-fluoronitrobenzene were added in sequence. The mixture was heated with stirring at 110 °C for 15 h and then precipitated into 300 mL of methanol yielded 14.13 g of the desired nitro compound **1** as yellow crystals in 98% yield; mp = 209−212 °C (lit. ref 24, 205−215 °C). IR (KBr): 1581, 1314 cm^{-1} (NO_2 stretch). ^1H NMR (400 MHz, DMSO-d_6, δ): 7.33 (t, 2H, H_e), 7.45 (t, 2H, H_d), 7.55 (d, 2H, H_c), 7.96 (d, 2H, H_b), 8.26 (d, 2H, H_f), 8.49 (d, 2H, H_a). ^{13}C NMR (100 MHz, DMSO-d_6, δ: 109.8 (C^5), 120.7 (C^7), 122.4 (C^8), 123.6 (C^9), 125.6 (C^2), 126.5 (C^6), 127.0 (C^3), 139.4 (C^{10}), 143.0 (C^1) 148.8 (C^4). Anal. Calcd for $C_{18}H_{12}N_2O_2$ (288.30): C, 74.99%; H, 4.20%; N, 9.72%. Found: C, 74.96%; H, 4.27%; N, 9.75%.



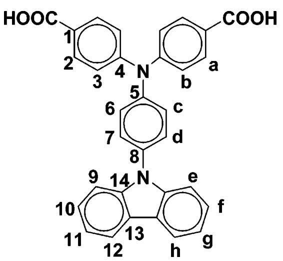
*N-(4-Aminophenyl)carbazole (***2***)*. In a 500-mL round-bottom flask, 25.95 g (0.09 mol) of nitro compound **1** and 0.9 g of palladium 10 wt % on activated carbon (Pd/C) were dissolved/suspended in 270 mL of ethanol. The suspension solution was heated to reflux, 23 mL of hydrazine monohydrate was added slowly to the mixture, and then the solution was stirred at reflux temperature for 10 h. After cooling to room temperature, the solution was filtered to remove the catalyst. The filtrate was evaporated under reduced pressure to dryness, and the obtained yellow viscous product was used for the next step without further purification. IR (KBr): 3350, 3430 cm^{-1} (N−H stretch). ^1H NMR (400 MHz, DMSO-d_6, δ): 5.44 (s, 2H, NH_2), 6.80 (d, 2H, H_a), 7.17−7.26 (m, 6H, $H_b + H_c + H_e$), 7.40 (t, 2H, H_d), 8.17 (d, 2H, H_f). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 109.8 (C^5), 114.9 (C^2), 119.4 (C^7), 120.5 (C^8), 122.8 (C^9), 125.1 (C^4), 126.7 (C^6), 127.9 (C^3), 141.1 (C^{10}), 148.8 (C^1). Anal. Calcd for $C_{18}H_{14}N_2$ (258.32): C, 83.69%; H, 5.46%; N, 10.84%. Found: C, 83.39%; H, 5.50%; N, 10.74%.



*4,4′-Dicyano-4″-N-carbazolyltriphenylamine (***3***)*. A mixture of 5.52 g (0.23 mol) of sodium hydride and 200 mL of *N*,*N*-dimethylformamide (DMF) was stirred, under nitrogen, at room temperature for about 30 min, and then 23.25 g (0.09 mol) of compound **2** were added. After the evolution of hydrogen was complete, 21.80 g (0.18 mol) of 4-fluorobenzonitrile were added and the temperature maintained for 10 h at 150 °C. Next, the reaction mixture was poured into water, the crude product collected by filtration, and purified by crystallization from toluene to give yellowish needles 14.20 g (yield: 34%); mp = 305−309 °C by DSC at 10 °C /min. IR (KBr): 2219 cm^{-1} (C≡N). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.23 (d, 4H, H_b), 7.31−7.39 (m, 4H, $H_g + H_c$), 7.43−7.50 (m, 4H, $H_f + H_e$), 7.59−7.64 (m, 6H, $H_a + H_d$), 8.15 (d, 2H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 106.3 (C^1), 109.4 (C^9), 118.8 (−CN), 120.2 (C^{11}), 120.7 (C^{12}), 123.3 (C^3), 123.6 (C^{13}), 126.0 (C^{10}), 127.8 (C^6), 128.5 (C^7), 133.8 (C^2), 135.5 (C^8), 140.8 (C^{14}), 143.7 (C^5), 150.0 (C^4). Anal. Calcd for $C_{32}H_{20}N_4$ (460.58): C, 74.99%; H, 4.20%; N, 9.72%. Found: C, 74.96%; H, 4.27%; N, 9.81%.



*4,4′-Dicarboxy-4″-N-carbazolyltriphenylamine (***4***)*. A mixture of 20.20 g of potassium hydroxide and 11.51 g of the dinitrile compound **3** in 80 mL of ethanol and 30 mL of distilled water was stirred at about 100 °C until no further ammonia was generated. The time taken to reach this stage was about 5−6 days. The solution was cooled, and the pH value was adjusted by hydrochloric acid to near 3. The yellowish precipitate formed was collected by filtration and purified by recrystallization from acetic acid to give 6.59 g (53% yield) of the pure diacid (mp = 334−337 °C by DSC at 10 °C/min). IR (KBr): 1702 (C═O), 2700−3400 cm^{-1} (O−H). ^1H NMR (400 MHz, DMSO-d_6, δ): 7.20 (d, 4H, H_b), 7.28 (t, 2H, H_g), 7.37 (d, 2H, H_c), 7.40−7.50 (m, 6H, $H_e + H_f$), 7.59 (d, 2H, H_d), 7.95 (d, 2H, H_a), 8.20 (d, 2H, H_h), 12.75 (br, 2H, −COOH). ^{13}C NMR (100 Hz, DMSO-d_6, δ): 109.8 (C^9), 119.9 (C^{11}), 120.2 (C^{12}), 122.2 (C^3), 122.6 (C^{13}), 125.2 (C^1), 126.0 (C^{10}), 127.2 (C^6), 128.0 (C^7), 131.0 (C^2), 133.4 (C^8), 140.0 (C^{14}), 142.3 (C^5), 150.4 (C^4), 167.0 (C═O). Anal. Calcd for $C_{32}H_{22}N_2O_4$ (498.53): C, 77.10%; H, 4.45%; N, 5.62%. Found: C, 76.98%; H, 4.52%; N, 5.71%.



Polymer Synthesis. *Preparation of Poly(amine-amide)s* ***5a***−**g**. The synthesis of poly(amine-amide) **5a** is used as an example to illustrate the general synthetic route. The typical procedure is as follows. A mixture of 0.62 g (1.25 mmol) of the dicarboxylic acid monomer **4**, 0.14 g (1.25 mmol) of *p*-phenylenediamine, 0.15 g of calcium chloride, 0.9 mL of triphenyl phosphate (TPP), 0.6 mL of pyridine, and 2.5 mL of *N*-methyl-2-pyrrolidone (NMP) was heated with stirring at 105 °C for 3 h. The resulting viscous polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried at 150 °C for 15 h in vacuo. Precipitations from *N*,*N*-dimethylacetamide (DMAc) into methanol were carried out twice for further purification. The inherent viscosity of the obtained poly(amine-amide) was 0.61 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. The IR spectrum of **5a** (film) exhibited characteristic amide absorption bands at 3316 (N−H stretching), 1663 cm^{-1} (amide carbonyl). Anal. Calcd for $(C_{38}H_{26}N_4O_2)_n$ $(570.65)_n$: C, 77.98%; H, 4.59%; N, 9.82%. Found: C, 77.68%; H, 4.68%; N, 9.88%. The other poly(amine-amide)s were prepared by an analogous procedure.

Preparation of Polymer Films. A solution of polymer was made by dissolving about 0.60 g of the poly(amine-amide) 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 remove most of the solvent. The cast film was then released from the glass substrate and was further dried in vacuo at 180 °C for 8 h. The obtained films were about 50−70 μm in thickness and were used for tensile tests, solubility tests, and thermal analyses.

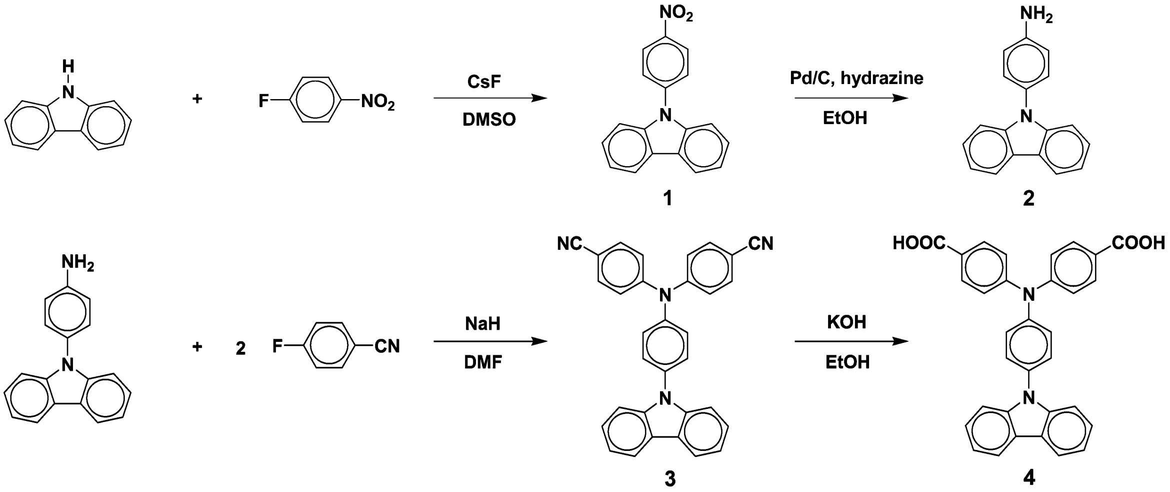
Characterization. Infrared spectra were recorded on a Perkin Elmer RXI FT-IR spectrometer. Elemental analyses were run in an Elementar VarioEL-III. ^{1}H and ^{13}C NMR spectra were measured on a Varian Unity Inova 400 FT-NMR system. The inherent viscosities were determined at 0.5 g/dL concentration using a 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. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress−strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long), and an average of at least three replicates was used. 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 Perkin Elmer Pyris Diamond DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm^3/min). Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.7 cm × 0.5 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. 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 an Ag/AgCl reference electrode. Absorption spectra were measured using an HP 8453 UV−visible spectrophotometer. Photoluminescence spectra were obtained from a Jasco FP-6300 spectrofluorometer.

Results and Discussion

Synthesis and Characterization. The new aromatic dicarboxylic acid having bulky pendent carbazole group, 4,4′-dicarboxy-4′′-*N*-carbazolyltriphenylamine (**4**)**,** was synthesized in four steps starting from the coupling reaction of carbazole with 4-fluoronitrobenzene (Scheme 1). *N*-(4-Aminophenyl)-carbazole (**2**) was prepared by the cesium-fluoride-mediated arylation of carbazole with 4-fluoronitrobenzene, followed by hydrazine Pd/C-catalyzed reduction of the intermediate compound, *N*-(4-nitrophenyl)carbazole (**1**). The double-coupling reaction of the conjugate base of **2** (1.0 equiv) with 4-fluorobenzonitrile (2.0 equiv) produced 4,4′-dicyano-4′′-*N*-carbazolyltriphenylamine (**3**)**.** The alkaline hydrolysis of the dinitrile compound **3** afforded the target dicarboxylic acid monomer **4**. Elemental analysis, IR, ^{1}H, and ^{13}C NMR spectroscopic techniques were used to identify the structures of the intermediate compounds **1**−**3** and the dicarboxylic acid monomer **4**. The IR spectra of dinitrile compound **3** gave a characteristic sharp band at 2219 cm^{-1} peculiar to the cyano group. After hydrolysis, the characteristic absorption of the cyano group disappeared, and the carboxylic acid group showed a typical carbonyl absorption band at 1674 cm^{-1} (C═O stretching) together with the appearance of broad bands around 2700−3400 cm^{-1} (O−H stretching). Figures 1 and 2 illustrate the ^{1}H NMR and ^{13}C NMR spectra of compounds **3** and **4**, respectively. Assignments of each carbon and proton are assisted by the two-dimensional (2D) NMR spectra (Figures 3 and 4), and these spectra agree well with the proposed molecular structures of **3** and **4**. The ^{13}C NMR spectra confirm that the cyano groups were completely converted into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 118.8 ppm and by the appearance of the carbonyl peak at 167.0 ppm. Other important evidence of this change is the shifting of the carbon resonance signals of C^1 adjacent to the cyano or carboxyl group. The C^1 carbons of dinitrile **3** resonated at a higher field (106.3 ppm) than the other aromatic carbons because of the anisotropic shielding by the π electrons of C≡N. After hydrolysis, the resonance peak of C^1 shifted to a lower field (125.2 ppm) because of the lack of an anisotropic field. A full assignment of the resonances of the aromatic protons and carbons was assisted by the two-dimensional COSY experiments. Figure 3 shows the H−H COSY spectrum for the aromatic region of dicarboxylic acid monomer **4**. The correlated pairs of AB doublets at 7.95/7.20 ppm and 7.59/7.36 ppm can be easily assigned to the protons a−d on the triphenylamine core. The aromatic protons at the 4 positions (protons, h) of the carbazole unit appear at the most downfield (8.20 ppm) as a doublet. Accordingly, the connected triplet signal at 7.28 ppm is assigned to the protons, g. The complicated resonances in the region of 7.40−7.50 ppm are assigned to the interconnected protons, e, (as a doublet) and protons, f, (as a triplet), in which the triplet of protons, f, is also connected with the triplet signal at 7.28 ppm arising from protons, g. There are 15 resonance signals in the ^{13}C NMR spectrum of compound **4** due to one carbonyl carbon and 14 aromatic carbons. In the aromatic region, five resonance peaks at 150.4, 142.3, 140.0, 133.4, and 125.2 are peculiar to quaternary carbons. The other aromatic ^{13}C signals are well connected with the corresponding protons, as shown in the C−H COSY spectrum (Figure 4).

A series of new aromatic poly(amine-amide)s with pendent carbazole units were prepared by the direct polycondensation reactions of the dicarboxylic acid monomer **4** with various aromatic diamines using TPP and pyridine as condensing agents[25] (Scheme 2)**.** All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured with stirring into methanol. These poly(amine amide)s were obtained in almost quantitative yields, with inherent values in the range of 0.36−0.61 dL/g (Table 1). The chemical structures of poly(amine-amide)s were confirmed by elemental, IR, and NMR analyses. As shown in Table 1, the elemental analysis results of these polymers generally agreed

Scheme 1. Monomer Synthesis



with the calculated values for the proposed structures. Structural features of these poly(amine-amide)s were verified by FTIR spectra based on characteristic absorption bands observed around 3300 (N−H stretching) and 1650 cm^{-1} (C═O stretching). Solution ^{1}H and ^{13}C NMR spectra in DMSO-d_6 confirmed the chemical structures of the prepared poly(amine-amide)s with amide proton chemical shifts observed in the region of 10.1−10.2 ppm and the amide carbonyl peaks around 165 ppm.

The packing of these poly(amine-amide)s in the solid state was found to be amorphous by X-ray diffraction experiments. The solubility behavior of poly(amine-amide)s was tested qualitatively, and the results are presented in Table 2. All the poly(amine-amide)s were highly soluble in polar solvents such as NMP, and the high solubility can be attributed in part to the introduction of propeller-shaped triphenylamine core and bulky pendent carbazole group in the repeat unit. Thus, all these polymers can be readily processed from solution. Flexible and tough films can be obtained via solvent casting. The cast films showed tensile strengths, elongations to break, and initial moduli in the ranges of 66−95 MPa, 4−63% and 1.9−2.7 GPa, respectively (Table 3). The thermal behavior data of the poly(amine-amide)s determined by TGA and DSC are summarized in Table 4. Typical TGA curves of a representative poly(amine-amide) **5g** in both air and nitrogen atmospheres are shown in Figure 5. All the poly(amine-amide)s exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen,

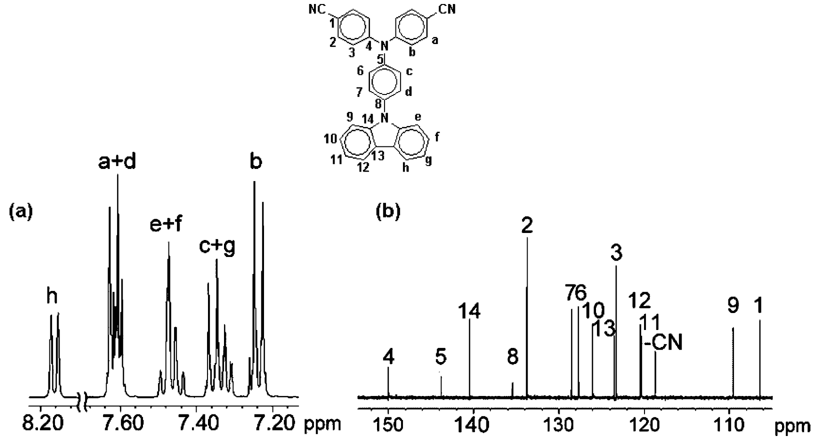


Figure 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound **3** in CDCl$_3$.

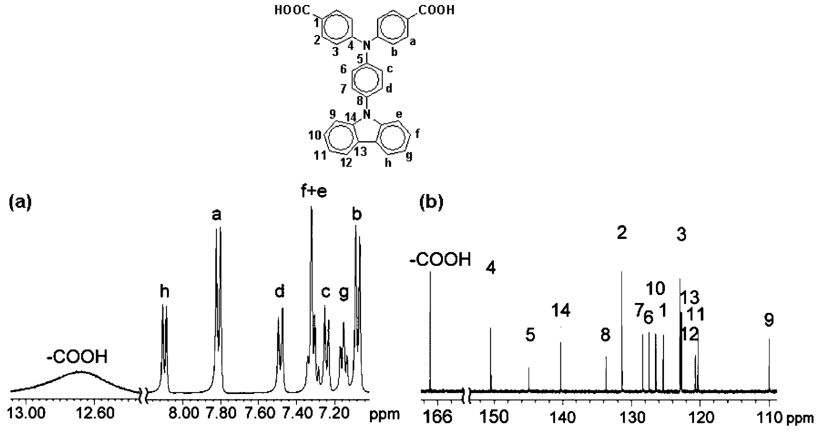


Figure 2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of compound **4** in DMSO-d_6.

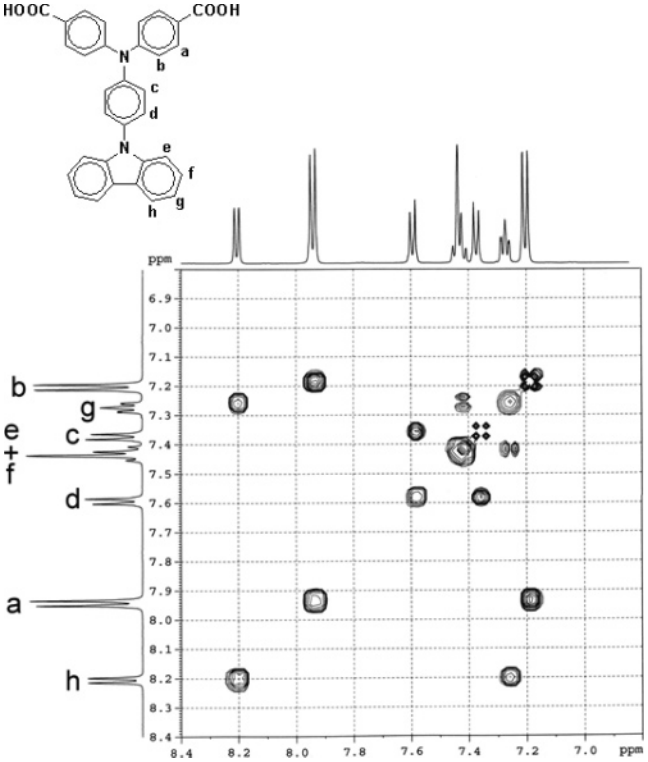


Figure 3. H−H COSY spectrum of 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine in DMSO-d_6.

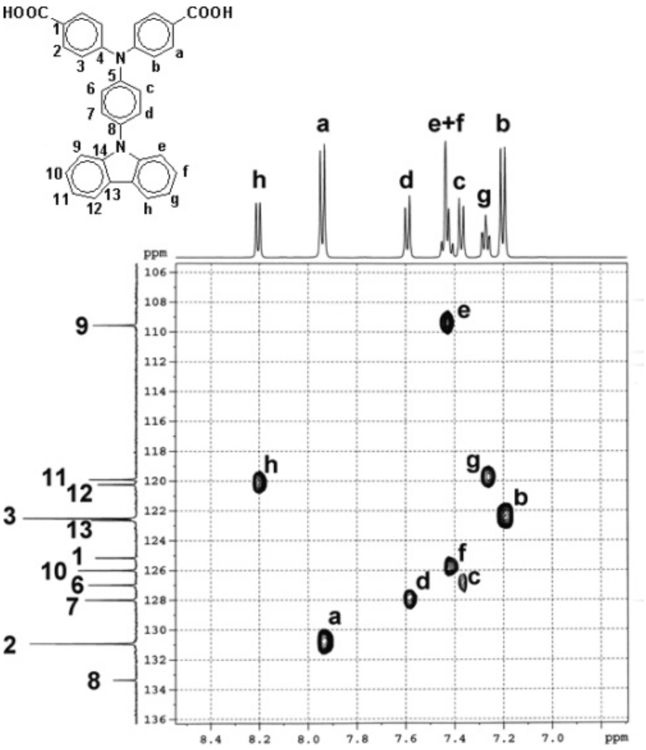


Figure 4. C−H HMQC spectrum of 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine in DMSO-d_6.

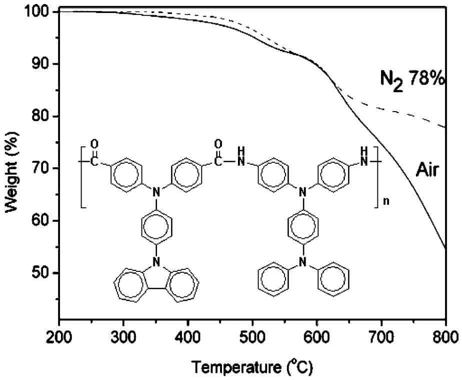


Figure 5. TGA thermograms of poly(amine-amide) **5g** at a scan rate of 20 °C/min.

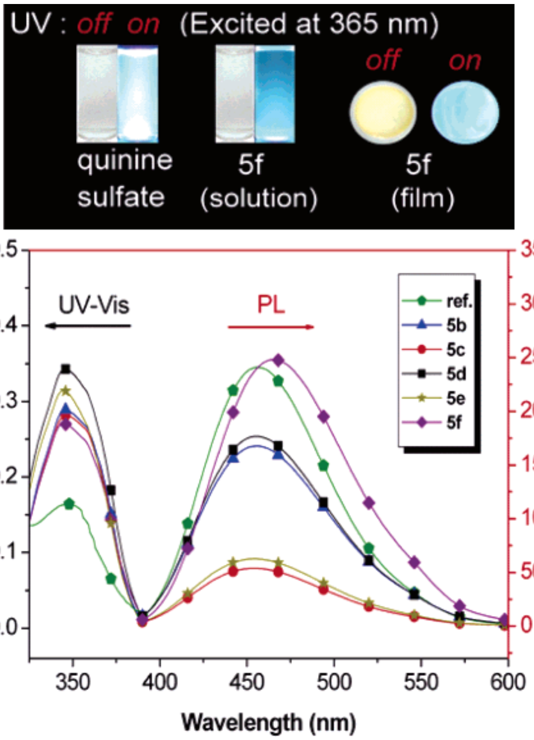


Figure 6. UV−Vis absorption and PL spectra of some poly(amine-amide)s in NMP at a concentration of ca. 1 × 10^{-5} M. Reference: quinine sulfate (ca. 1 × 10^{-5} M) in 1 N H_2SO_4.

and the 10% weight-loss temperatures in nitrogen and air were recorded in the range of 556−618 and 533−612 °C, respectively. The amount of carbonized residue (characteristic yield) of these polymers in nitrogen atmosphere was more than 65% at 800 °C. The high characteristic yields of these polymers can be ascribed to their high aromatic content. The T_g values of the polymers were observed in the range of 229−322 °C by DSC and generally increased with decreasing conformational flexibility of the diamine used. Such a high value of T_g, which should prevent morphological changes and suppress the formation of aggregates and excimers during annealing or passage of current, is desirable for polymers that are used as emissive or hole-transporting materials for light-emitting applications. All of the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result also supports the amorphous nature of these carbazole-containing polymers. It is evident that the presence of propeller-like triphenylamine units and bulky carbazole pendant groups hinders close packing of the polymer chains and suppresses their crystallizability.

Optical Properties. Figure 6 illustrates the UV−vis absorption and PL spectra of dilute solutions of some representative poly(amide-amide)s; Table 5 summarizes the spectral data of all the synthesized polymers. For comparison, Figure 6 also presents the absorption and PL spectra of the solution of quinine sulfate in H_2SO_4 as a reference. In NMP solutions, polymers **5a−g** exhibited shape-similar absorption bands having their λ_{max}

Scheme 2. Polymer Synthesis

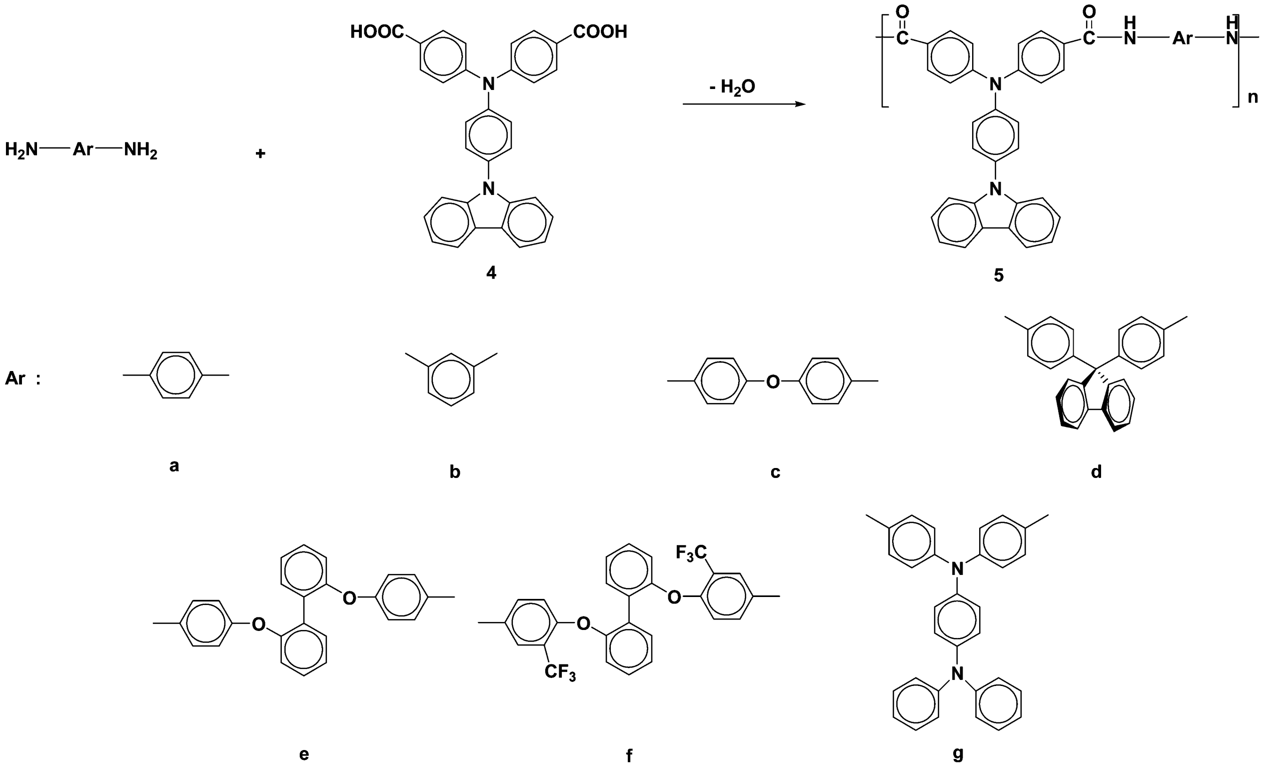


Table 1. Inherent Viscosity and Elemental Analysis of Poly(amine-amide)s

poly(amine-amide)s		elemental analysis (%) of poly(amine-amide)s				
code	η_{inh}[a] (dL/g)	formula (molecular weight)		C	H	N
5a	0.61	$(C_{38}H_{26}N_4O_2)_n$	calcd	77.98	4.59	9.82
		$(570.65)_n$	found	77.68	4.68	9.88
5b	0.36	$(C_{38}H_{26}N_4O_2)_n$	calcd	77.98	4.59	9.82
		$(570.65)_n$	found	77.79	4.70	9.73
5c	0.60	$(C_{44}H_{30}N_4O_3)_n$	calcd	79.74	4.56	8.45
		$(662.23)_n$	found	78.71	4.75	8.44
5d	0.44	$(C_{56}H_{38}N_4O_2)_n$	calcd	84.19	4.79	7.01
		$(798.30)_n$	found	82.95	4.91	7.06
5e	0.50	$(C_{56}H_{38}N_4O_4)_n$	calcd	80.95	4.61	6.74
		$(830.29)_n$	found	79.59	4.69	6.69
5f	0.45	$(C_{58}H_{36}F_6N_4O_4)_n$	calcd	72.05	3.75	5.79
		$(966.26)_n$	found	71.63	3.86	5.59
5g	0.46	$(C_{62}H_{44}N_6O_4)_n$	calcd	82.46	4.69	9.31
		$(904.35)_n$	found	81.63	4.88	9.28

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

Table 2. Solubility of Poly(amine-amide)s

polymer code	solubility[a]						
	NMP	DMAc	DMF	DMSO	*m*-cresol	THF	$CHCl_3$
5a	+	+	+	+	+	−	−
5b	+	+	+	+	+	−	−
5c	+	+	−	−	−	−	−
5d	++	++	++	++	+	−	−
5e	++	++	++	++	+	++	−
5f	++	++	++	++	+	++	++
5g	++	++	++	−	−	−	−

[a] The solubility was determined by using 1 mg sample in 1 mL of solvent. ++: soluble at room temperature; +: soluble on heating; −: insoluble even on heating.

Table 3. Mechanical Properties of Poly(amine-amide) Films

polymer	tensile strength (MPa)	elongation at break (%)	initial modulus (GPa)
5a	87	12	2.7
5b	66	4	1.9
5c	77	63	1.9
5d	95	14	2.5
5e	82	6	2.5
5f	91	9	2.6
5g	73	5	2.1

at 346−361 nm, which can be attributed to the $\pi-\pi^*$ transitions derived from the polymer backbones. The fluorescence spectra of the poly(amine-amide)s **5a**−**f** in NMP solutions exhibited emission maxima at 454−465 nm. The fluorescence quantum yield (Φ_f) of **5f** (0.46) measured in NMP is the highest among the series polymers and is much higher than that of structurally similar **5e** (0.10). This may be the result of the presence of bulky, electron-withdrawing trifluoromethyl ($-CF_3$) substituents in **5f**, which effectively restrict intra- and intermolecular charge transfer (CT) interactions. On the contrary, polymer **5g** exhibited significantly less detectable fluorescence ($\Phi_f = \sim 10^{-3}$) than that of the other polymers. The weak fluorescence of **5g** might be attributed to introduction of a higher HOMO energy level and electron-donating diamine structure, which resulted in nonradiative decay by the formation of CT or photoinduced electron transfer effect between the diacid and diamine moieties. The solid-state emission spectra were similar to those recorded from the NMP solution. Although the solid-state emission for some of poly(amine-amide)s was found to be slightly red-shifted from the corresponding solution emission, the emission remained in the blue region. The photoluminescence images of the polymer solution and thin film of **5f** under UV irradiation are also shown in Figure 6, and both of them showed strong fluorescent blue light. The cutoff wavelengths of the poly(amine-amide) films (absorption edge; λ_0) in the range of 407−461 nm from the UV−vis transmittance spectra are also included in Table 5. It revealed that most of the poly(amine-amide)s show lower λ_0 values in the range of 407−420 nm due to the lower capability of intermolecular CT interactions. This is consistent

Table 4. Thermal Properties of Poly(amine-amide)s

polymer	T_g (°C)[a]	T_d at 5% weight loss (°C)[b]		T_d at 10% weight loss (°C)[b]		char yield (wt %)[c]
		N_2	air	N_2	air	
5a	322	501	491	577	572	70
5b	307	478	430	571	533	78
5c	300	508	470	556	545	75
5d	315	528	512	618	612	67
5e	229	516	514	568	559	70
5f	*d*	496	465	558	546	65
5g	269	517	505	600	590	78

[a] Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C. [b] Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm^3/min. [c] Residual weight percentage at 800 °C in nitrogen. [d] No discernible T_g was observed.

with the fact that the films of most polymers appeared as low-color and high optical transparency, as shown in Table 5.

Electrochemical Studies. Cyclic voltammetric (CV) data for the poly(amine-amide)s are given in Table 6, and representative cyclic voltammograms of polymers **5d** and **5g** are shown in Figure 7. The poly(amine-amide)s **5a−f** revealed one reversible redox couple at half-wave potential ($E_{1/2}$) of 1.11−1.18 V and one irreversible oxidation redox wave at $E_{p,a} = 1.72-1.85$ V under an anodic sweep. The first electron removal for poly(amine-amide) **5d** is assumed to occur at the nitrogen atom on the main chain triphenylamine unit, which is more electron-rich than the nitrogen atom on the pendent carbazolyl moiety at $E_{p,a} = 1.72$ V. Thus, the first stable cationic radical of poly(amine-amide)s$^{+\bullet}$ should be formed by the first oxidation at the nitrogen atom of triphenylamine unit. The energy levels of the HOMO and LUMO of the investigated poly(amine-amide)s can be estimated from the oxidation onset (E_{onset}) or half-wave potentials ($E_{1/2}$) and the onset absorption wavelength of the UV−vis spectra, and the results are listed in Table 6. For example, the $E_{1/2}$ value for poly(amine-amide) **5d** has been determined as 1.18 V vs Ag/AgCl. The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{1/2}$ (Fc/Fc^+) is 0.44 V vs Ag/AgCl in CH_3CN. Assuming that the HOMO energy level for the Fc/Fc^+ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy level for poly(amine-amide) **5d** has been evaluated to be 5.54 eV. The high-lying HOMO energy level and reversible electrochemical oxidation of these polymers suggest that they have potential for use as hole injection and transport materials in EL devices.

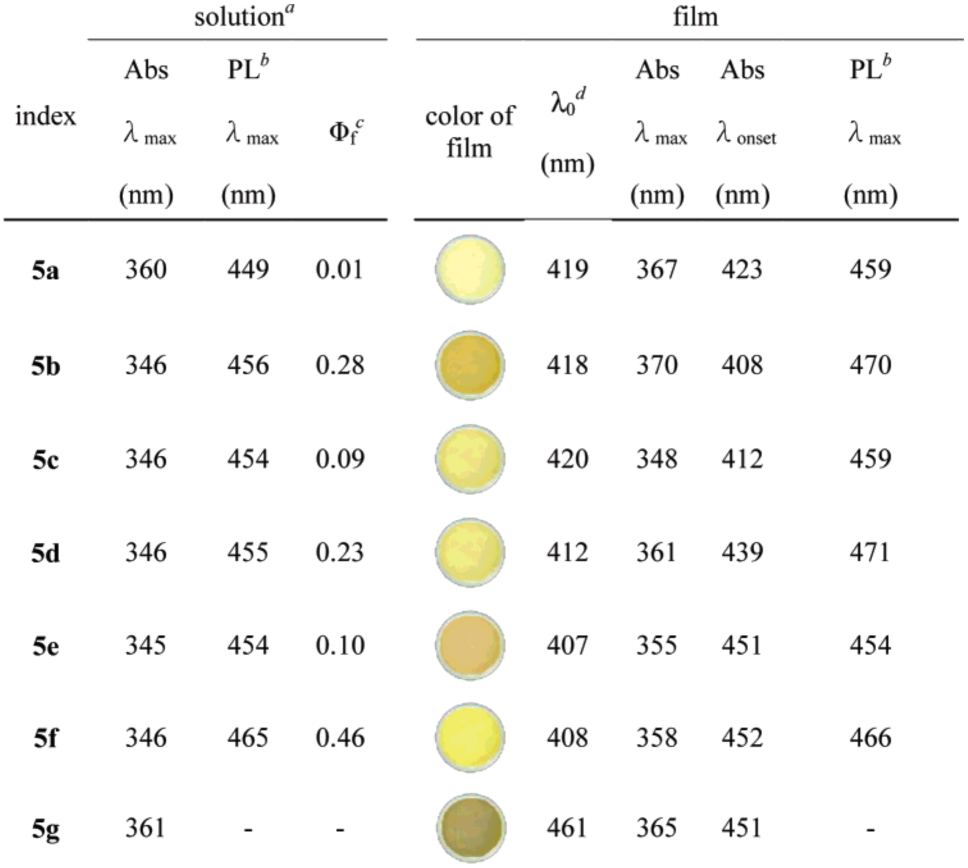
Table 6. Electrochemical Properties of Poly(amine-amide)s

index	oxidation potential, $E_{1/2}$ (V) (vs Ag/AgCl)				E_{gap}[a] (eV)	HOMO[b] (eV)	LUMO[c] (eV)
	1st	2nd	3rd	4th			
5a	1.11	(1.83)[d]			2.93	5.47	2.54
5b	1.14	(1.82)[d]			3.04	5.50	2.46
5c	1.11	(1.74)[d]			3.01	5.47	2.46
5d	1.18	(1.72)[d]			2.82	5.54	2.72
5e	1.11	(1.78)[d]			2.75	5.47	2.72
5f	1.15	(1.85)[d]			2.74	5.51	2.77
5g	0.64	0.98	1.18	(1.76)[d]	2.75	5.00	2.25

[a] The data were calculated by the equation: gap = 1240/Abs λ_{onset}. [b] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). [c] LUMO = HOMO − E_{gap}. [d] Irreversible peak potential ($E_{p,a}$).

Spectroelectrochemical and Electrochromic Characteristics.. Spectroelectrochemical analysis of the poly(amine-amide)

Table 5. Optical Properties of Poly(amine-amide)s



index	solution[a] Abs λ_{max} (nm)	solution[a] PL[b] λ_{max} (nm)	solution[a] Φ_f[c]	film color of film	film λ_0[d] (nm)	film Abs λ_{max} (nm)	film Abs λ_{onset} (nm)	film PL[b] λ_{max} (nm)
5a	360	449	0.01		419	367	423	459
5b	346	456	0.28		418	370	408	470
5c	346	454	0.09		420	348	412	459
5d	346	455	0.23		412	361	439	471
5e	345	454	0.10		407	355	451	454
5f	346	465	0.46		408	358	452	466
5g	361	-	-		461	365	451	-

[a] Evaluated in NMP at a repeating unit concentration of ~ 1 × 10^{-5} M. [b] Excited at absorption λ_{max}. [c] Fluorescence quantum yield relative to 10^{-5} M quinine sulfate in 1 N $H_2SO_{4\,(aq)}$ ($\Phi_f = 0.55$) as a standard. [d] The cutoff wavelengths (λ_0) from the transmission UV/Vis absorption spectra of polymer films (thickness: 50−70 μm).

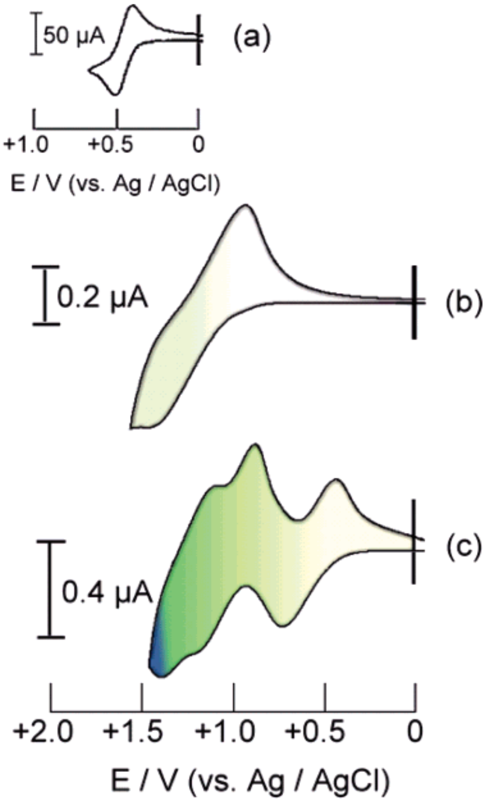


Figure 7. Cyclic voltammograms of (a) ferrocene, (b) poly(amine-amide) **5d**, and (c) poly(amine-amide) **5g** at 0.1 V/s in 0.1 M TBAP/acetonitrile.

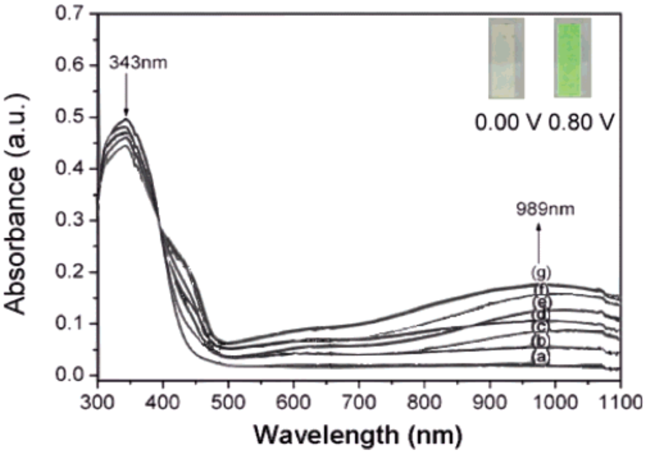


Figure 8. Changes in the UV−vis spectrum of a film of poly(amine-amide) **5g** on an ITO glass electrode at various potentials vs Ag/AgCl: (a) 0, (b) 0.55, (c) 0.60, (d) 0.65, (e) 0.70, (f) 0.75, and (g) 0.80 V (in an acetonitrile solution of 0.1 M TBAP as the supporting electrolyte).

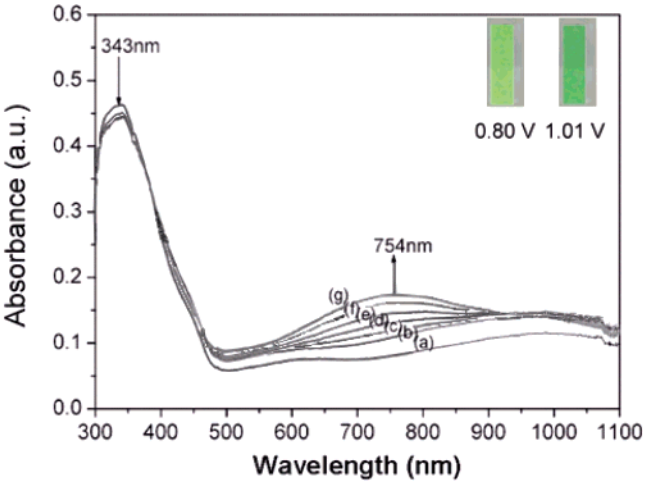


Figure 9. Changes in the UV−vis spectrum of a film of poly(amine-amide) **5g** on an ITO glass electrode at various potentials vs Ag/AgCl: (a) 0.80, (b) 0.83, (c) 0.86, (d) 0.90, (e) 0.94, (f) 0.97, and (g) 1.01 V (in an acetonitrile solution of 0.1 M TBAP as the supporting electrolyte).

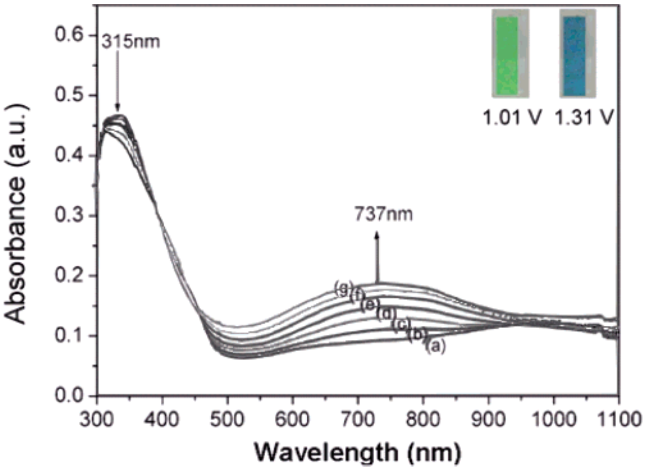


Figure 10. Changes in the UV−vis spectrum of a film of poly(amine-amide) **5g** on an ITO glass electrode at various potentials vs Ag/AgCl: (a) 1.01, (b) 1.07, (c) 1.13, (d) 1.18, (e) 1.23, (f) 1.28, and (g) 1.31 V (in an acetonitrile solution of 0.1 M TBAP as the supporting electrolyte).

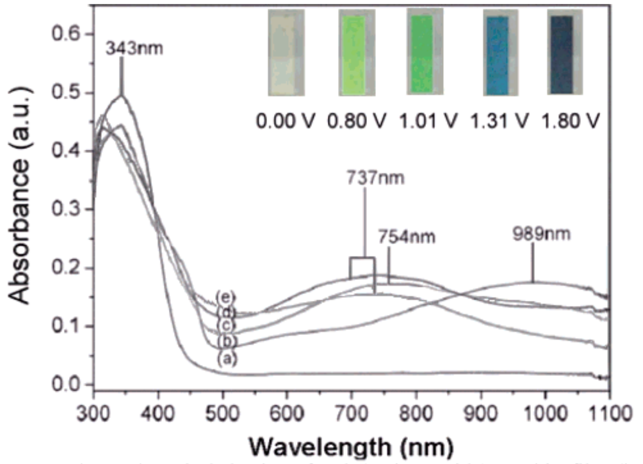


Figure 11. Electrochromic behavior of poly(amine-amide) **5g** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) at (a) 0, (b) 0.80, (c) 1.01, (d) 1.31, and (e) 1.80 V.

films was carried out on an ITO-coated glass substrate, and they showed multicolor electrochromic behavior when the applied potential was changed. The color of the polymers was changed from neutral pale yellowish to green and then to blue. The typical spectroelectrochemical spectra of poly(amine-amide) **5g** at various applied potentials are depicted in Figures 8−10. When the applied potential was increased positively from 0.00 to 0.80 V, the peak of characteristic absorbance at 343 nm, characteristic for poly(amine-amide) **5g**, decreased gradually, while one new band grew up at 989 nm due to the first electron oxidation. The new spectrum was assigned as that of the stable cationic radical poly(amine-amide)$^{+\bullet}$ and the film color changed from pale yellowish to green (as shown in Figure 8). When the potential was adjusted to more positive values, the second, third, and fourth oxidation generated electrochemically, and the spectral changes are shown as Figures 9−11, and the color of film **5g** became deep green to pale blue and then to deep blue. The stability and response time upon electrochromic switching

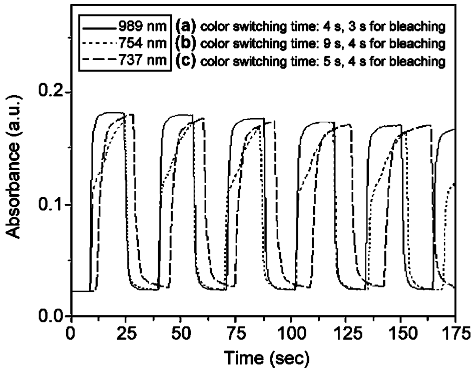
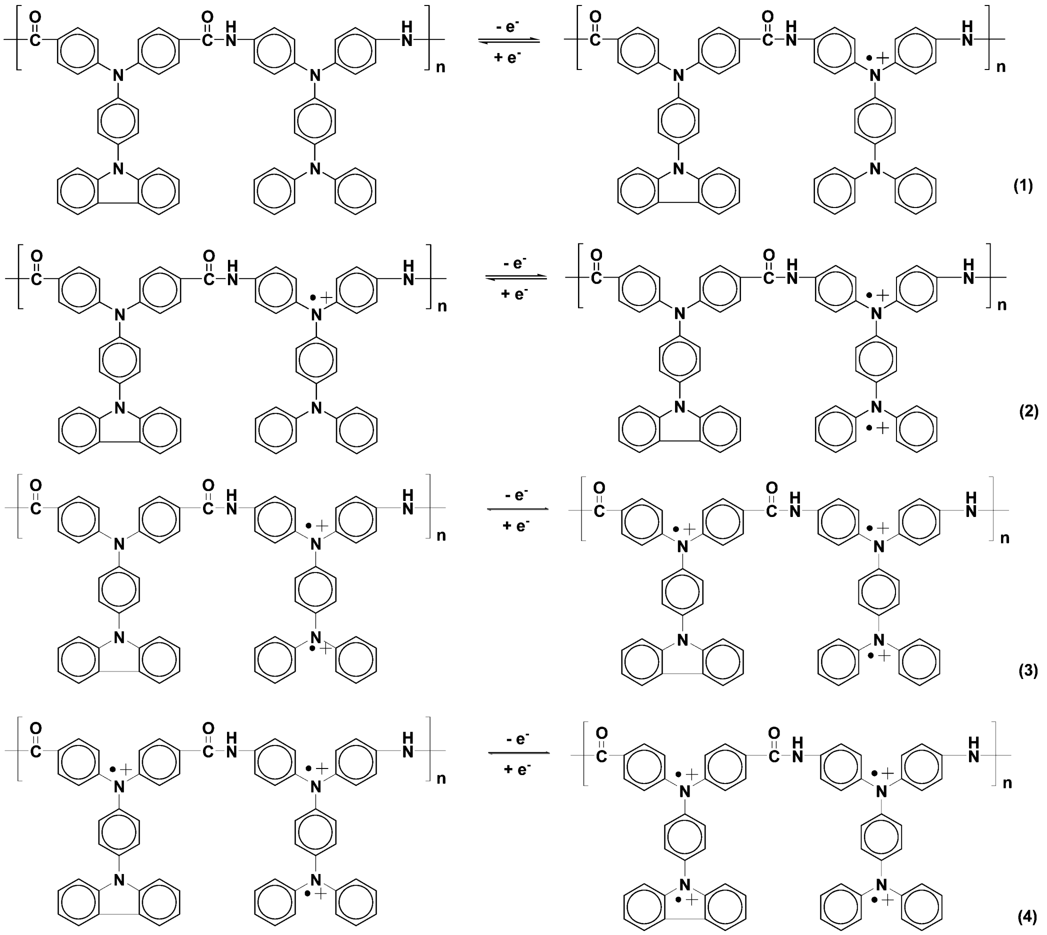


Figure 12. Potential step absorptometry of poly(amine-amide) **5g** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (a) (0 V ⇄ 0.80 V), (b) (0 V ⇄ 1.01 V), and (c) (0 V ⇄ 1.31 V), respectively.

of the polymer film between its neutral and oxidized forms was monitored (Figure 12). The color switching times were estimated by applying a potential step and the absorbance profiles followed. The switching time was defined as the time that required for reach 90% of the full change in absorbance after switching potential. Thin films of poly(amine-amide) **5g** would require 4 s at 0.80 V for switching absorbance at 989 nm and 3 s for bleaching. When the potential was set at 1.01 V, thin film **5g** would require about 9 s for coloration at 754 nm and 4 s for bleaching. With several continuous cyclic scans between 0.0 and 1.01 V, the polymer films still exhibited excellent stability of electrochromic characteristics. The anodic oxidation pathway of poly(amine-amide) **5g** was postulated as in the following:



Conclusion

The new carbazole-based aromatic diacid monomer, 4,4′-dicarboxy-4″-*N*-carbazolyltriphenylamine **4** was successfully synthesized in high purity and good yield. Novel blue-light-emitting aromatic poly(amine-amide)s bearing pendant *N*-phenylcarbazole units with high molecular weight were readily prepared from the newly synthesized dicarboxylic acid monomer and various aromatic diamines by direct phosphorylation polycondensation. All the poly(amine-amide)s were amorphous with high T_g and exhibited excellent thermal stability and useful mechanical properties (e.g., flexibility). The poly(amine-amide) **5f** showed low olor and high optical transparency and exhibited blue photoluminescence both in film state and in NMP solution with about a 46% quantum yield. The poly(amine-amide) films also showed good adherance behavior and were found to be electroactive. The multicolor electrochromic behavior of the polymer film **5g** exhibited from original pale yellowish to green and then to blue colors when various different potentials were applied. All obtained poly(amine-amide)s revealed good stability of electrochromic characteristics for the first oxidation state, changing color from the yellowish neutral form to the green oxidized forms when scanning potentials positively from 0.00 to 1.15 V. Thus, these poly(amine-amide)s can be employed as potential candidates in the development of dynamic electrochromic and EL devices due to their proper HOMO value, excellent thermal stability and reversible electrochemical behavior.

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