# Synthesis and Characterization of Novel Aromatic Polyamides Bearing CF₃, Quinoxaline-Anthraquinone Pendants: Study of Photophysical and Electrochemical Properties by Using Nanocomposite Electrode Paste

**Mousa Ghaemy, Arameh Masoumi, Seyed Mojtaba Amini Nasab, Marjan Hassanzadeh**
Polymer Chemistry Research Laboratory, Department of Chemistry, University of Mazandaran, Babolsar, 47416-95447, Iran

Correspondence to: M. Ghaemy (E-mail: ghaemy@umz.ac.ir)

**ABSTRACT:** A new aromatic diamine, 2,3-bis(4-(4-amino-2-(trifluoromethyl) phenoxy)phenyl)naphtho[2,3-f]quinoxaline-7,12-dione, was synthesized and fully characterized by using FTIR, $^1$H and $^{13}$C NMR, DEPT technique, and elemental analysis. A series of novel fluorescent anthraquinone-quinoxaline containing polyamides (PAs) with inherent viscosities of 0.39–0.62 dL/g was prepared by direct polycondensation of the diamine with various dicarboxylic acids. These PAs were readily soluble in many polar aprotic organic solvents and could be solution-cast into tough and flexible films. The PAs exhibited glass transition temperatures ($T_g$)s between 230 and 323°C, and 10% weight loss temperatures in the range of 362–433°C in $N_2$. All of the PAs have fluorescence emission in solution and in solid state with maxima around 452–510 nm and with the quantum yields in the range of 6–17%. Also, cyclic voltammetry (CV) method was used to study the electrochemical oxidation behavior of these polymers at the surface of a modified multiwalled carbon nanotube (MWCNT)s glassy electrode. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

## INTRODUCTION

One of the problems in high-temperature polymers such as aromatic PAs with excellent thermal and mechanical properties is their poor processability because of their high melting or softening temperatures and insoluble nature in most organic solvents.[1–3] Therefore, much effort has been made to modify the structure of PAs in order to have better properties in terms of both solubility and processability with protection of their high thermal stability. The successful approaches employed for those purposes include: introduction of flexible bonds (e.g., —O—, —SO₂—, etc.),[4–8] replacing symmetrical aromatic rings with unsymmetrical ones[9,10] and alicyclic units[11–13] into the polymer backbone or as bulky side groups[14–23] and forming a noncoplanar structure, thereby, do not allowing crystallization. It has also been recognized that the incorporation of aryl-ether linkages in aramids backbone generally impart an enhanced solubility and processability without substantial diminution of thermal properties. In recent years, considerable attention has been currently devoted to the fluorinated aromatic polyamides. It was found that the incorporation of flexible fluorinated groups into polyamide backbones resulted in great benefits for improving

polymer solubility and thermal stability as well as electrical and dielectric performance.[24–27]

As part of the efforts to gain the high-performance polymers with good solubility for advanced microelectronics applications, this article mainly reports the synthesis and characterization of a series of novel PAs bearing several functional groups in their backbone such as flexible ether linkage, and CF₃ and quinoxaline-anthraquinone pendants. These PAs were fully characterized and their properties such as solubility, thermal, photophysical, and electrochemical behavior were investigated.

## EXPERIMENTAL

### Materials and Measurements

All chemicals were purchased either from Merck or Fluka NMP was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves 4 Å. K₂CO₃ was dried for 24 h at 120°C under vacuum. All other reagents and solvents were used as received from commercial sources. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz and 100 MHz Bruker Advance DRX instrument respectively using DMSO-d₆ as solvent and tetramethyl silane as an internal

Additional Supporting Information may be found in the online version of this article.

standard. FTIR spectra were recorded using a Bruker Tensor 27 spectrometer on KBr pellets. The KBr pellets were prepared by mixing well dried powder of KBr and polymer sample (1% polymer) and a certain amount of this mixture was pressed under vacuum using 8 tons pressure. Elemental analysis was run in a Flash EA 1112 series. Melting point (uncorrected) was measured with a Barnstead Electrothermal engineering LTD 9200 apparatus. Thermogravimetric analysis (TGA) in the temperature range of 50–600°C was carried out with TGA-50 analyzer at a heating rate of 10°C/min in $N_2$. Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin Elmer Pyris 6 under $N_2$ (20 cm$^3$/min) at a heating rate of 10°C/min. The inherent viscosity of the polymers was determined for the solutions of 0.5 g/dL in NMP at constant temperature of 25°C by using an Ubbelohde viscometer. Ultraviolet-visible absorption and fluorescence emission spectra were recorded on a Cecil 5503 (Cecil Instruments, Cambridge, UK) and Perkin-Elmer LS-3B spectrophotometers (Norwalk, CT) (slit width = 2 nm), respectively, using a dilute polymer solution (0.20 g/dL) in NMP.

## Monomer Synthesis
### Synthesis steps of the target diamine are described below and outlined in Scheme 1

*Synthesis of 4, 4′-Dihydroxy Benzyl.* Into a 100-mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, 4,4′-dimethoxybenzyl (2 g, 0.0075 mol), aqueous HBr (15 mL, 48%) and glacial acetic acid (15 mL) were placed. The reaction mixture was refluxed for 24 h, after cooling to room temperature it was poured into 100 mL water. Ethyl acetate was added to the mixture to yield two phases of which the organic phase containing the product was separated and dried over magnesium sulfate for 12 h. The solvent was removed under reduced pressure and the obtained yellow precipitate was washed thoroughly with water and then dried in a vacuum oven at 80°C. Yield: 94% (1.7 g) and mp: 229–231°C. FTIR (KBr, cm$^{-1}$): 3400 (OH phenol stretching), 3045 (C—H aromatic stretching), 1646 (C=O stretching), 1576 (C=C stretching), 1223 (C—O stretching). $^1$H NMR (400 MHz, DMSO-$d_6$, δ ppm): 6.91-6.95 (d, $J$ = 8Hz, 4H, ArH), 7.73-7.77 (d, J = 8 Hz, 4H, ArH), 10.84 (s, 2H, OH phenol). Anal. Calcd for $C_{14}H_{10}O_4$: C 69.42%, H 4.13%. Found: C 69.37%, H 4.22%.

*Synthesis of 2,3-bis(4-hydroxyphenyl)naphtho[2,3-f]quinoxaline-7,12-dione )BNQ).* Into a 100-mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, acetic acid (15 mL), 4,4′-dihydroxy benzyl (1.21 g, 0.005 mol), and 1,2-diaminoanthraquinone (1.19 g, 0.005 mol) were placed. The mixture was refluxed for 24 h. After cooling to room temperature, the formed precipitate was collected by filtration, washed with water to give pale yellow needles, and dried in a vacuum oven at 80°C. Yield: 95% and mp: 353–356°C. FTIR (KBr, cm$^{-1}$): 3440 (OH phenol stretching), 3045 (C—H aromatic stretching), 1664 (C=O stretching), 1606 (C=N stretching), 1274 (C—O stretching). $^1$H NMR (400 MHz, DMSO-$d_6$, δ ppm): 6.79 (d, $J$ = 8Hz, 4H, ArH), 7.48 (d, $J$ = 8Hz, 2H, ArH), 7.55 (d, $J$ = 8Hz, 2H, ArH), 7.89 (t, $J$ = 8Hz, 2H, ArH), 8.14 (d, $J$ = 8Hz, 2H, ArH), 8.34 (dd, $J$ = 8Hz, 2H, ArH), 9.95 (s,1H, OH phenol), 9.97 (s, 1H, OH phenol). $^{13}$C NMR ( 100 MHz, DMSO-$d_6$, δ):115.50, 115.67, 123.91, 125.96, 126.52, 126.90, 128.92, 129.11, 129.53, 131.72, 132.12, 134.11, 134.58, 134.77, 135.05, 135.09, 137.76, 142.44, 153.56, 154.38, 159.39, 159.46, 182.72, 183.16. DEPT Technique (135 MHz, DMSO-$d_6$, δ):115.50, 115.67, 125.96, 126.52, 126.90, 131.72, 132.12, 134.11, 134.74, 135.09. Anal. Calcd for $C_{28}H_{16}N_2O_4$: C 75.67%, H 3.60%, N 6.30%. Found: C 75.59%, H 3.68%, N 6.29%.

*Synthesis of 2,3-bis(4-(4-nitro-2-(trifluoromethyl)phenoxy)phenyl)naphtho[2,3-f]quinoxaline-7,12-dione (BNNQ).* Into a 100-mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, BNQ (2.22 g, 0.005 mol) and 2-chloro-5-nitrobenzotrifluoride (2.25 g, 0.01 mol) were dissolved in 10 mL DMAc. Potassium carbonate (1.4 g, 0.01 mol) was added to the solution and after 30 min stirring at room temperature the mixture was heated at 110 °C for 12 h. The mixture was poured in 100 mL water to give yellow precipitate which was filtered, washed with water, and dried in a vacuum oven at 80°C. Yield: 95% (3.9 g) and the product turned into a black mass at 210 °C. FTIR (KBr, cm$^{-1}$): 1332, 1536 (NO2 symmetric and dissymmetric stretching) and 1240 (C—O stretching). $^1$H NMR (400 MHz, DMSO-$d_6$, δ ppm): 7.14 (q, $J$ = 8Hz, 2H, ArH), 7.37 (d, $J$ = 8 Hz, 4H, ArH), 7.78 (d, $J$ = 8 Hz, 2H, ArH), 7.82(d, $J$ = 8Hz, 2H, ArH), 7.94 (d, $J$ = 8 Hz, 2H, ArH), 8.18 (d, $J$ = 8 Hz, 2H, ArH), 8.43 (d, $J$ = 8Hz, 2H, ArH), 8.50 (d, $J$ = 8Hz, 1H, ArH), 8.52 (d, $J$ = 8 Hz, 1H, ArH), 8.52 ( s, 2H, ArH). $^{13}$C NMR ( 100 MHz, DMSO-$d_6$, δ):118.91, CF$_3$ (119.47, 119.79, 121.35, 124.06), 120.78, 120.89, 123.91, 123.96, 124.06, 126.66, 127.02, 129.30, 130.60, 132.15, 132.90, 133.21, 134.34, 135.08, 135.26, 135.31, 135.65, 135.93, 136.24, 138.30, 142.34, 142.37, 142.80, 153.27, 154.07, 155.34, 155.40, 160.22, 182.73, 183.17. DEPT Technique (135 MHz, DMSO-$d_6$, δ): 118.90, 120.78, 120.89, 123.91, 123.96, 126.66, 127.01, 130.60, 132.90, 133.21, 134.34, 135.26, 135.31. Anal. Calcd for $C_{42}H_{20}N_4O_8F_6$: C 61.31%, H 2.43%, N 6.81%. Found: C 61.21%, H 2.55%, N 6.84%.

*Synthesis of 2,3-bis(4-(4-amino-2-(trifluoromethyl)phenoxy)phenyl)naphtho[2,3-f]quinoxaline-7,12-dione (BANQ).* In a 100-mL round-bottom flask equipped with stirring bar and a reflux condenser, a mixture of BNNQ (4.42 g, 0.005 mol) and Pd/C (0.1 g, 10%) were dispersed in 30 mL ethanol. The suspension was heated to reflux, and 6 mL hydrazine monohydrate was added slowly to the mixture. After a further 8 h reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to give a brownish precipitate which was crystallized in acetonitrile, filtered, and dried in a vacuum oven at 80°C. Yield: 81% (3.10 g) and the product turned into a black mass at 170°C. FTIR (KBr, cm$^{-1}$): 3384, 3274 (N—H stretching), 1668 (C=O stretching), 1232 (C—O stretching). $^1$H NMR (400 MHz, DMSO-$d_6$, δ ppm): 5.55 ( s, 4H, NH$_2$), 6.85-7.00 ( m, 10H, ArH), 7.57 (d, $J$ = 8Hz, 2H, ArH), 7.61 (d, $J$ = 8 Hz, 2H, ArH), 7.87(m, 2H, ArH), 8.11 (d, $J$ = 8 Hz, 2H, ArH), 8.33 (d, $J$ = 8 Hz, 1H, ArH), 8.38 (d, $J$ = 8Hz, 1H, ArH). $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 1 (111.15, 111.21), 2 (116.52, 116.58), 3 (118.96), 4 (124.04), 5 (124.12), 6 (125.04, 125.22, 125.28, 125.40), 7 (126.64), 8 (126.98), 9 (129.25), 10 (131.94), 11 (132.22), 12 (132.25), 13 (132.33), 14 (132.79), 15 (134.27), 16 (135.16), 17 (135.24), 18 (135.33), 19 (138.07), 20 (141.87), 21
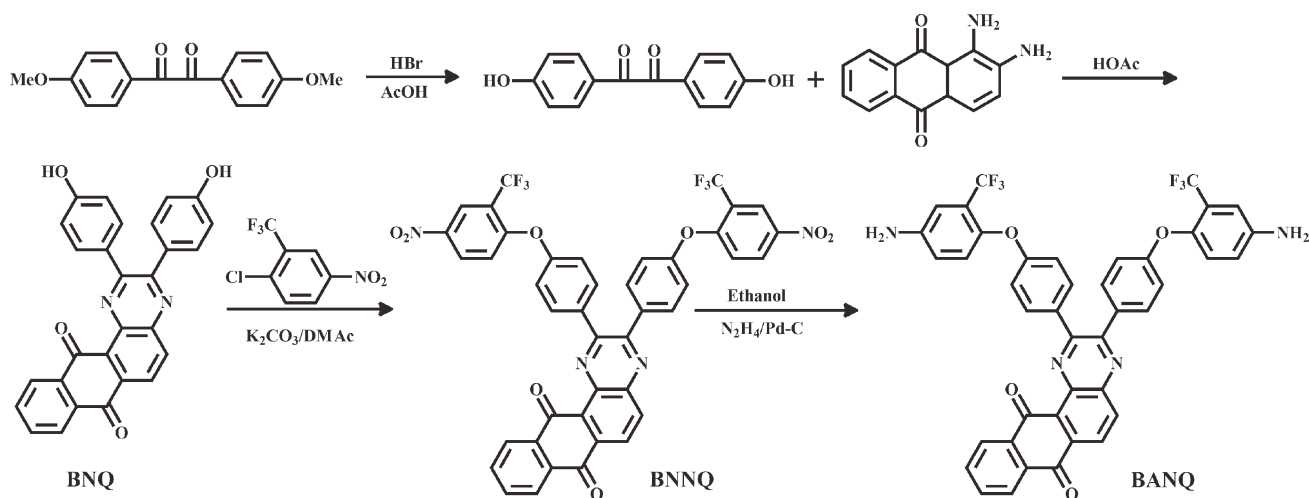
**Scheme 1.** Synthetic procedure for preparation of target diamine.

(142.87), 22 (146.71), 23 (146.76), 24 (153.44), 25 (154.28), 26 (160.16), 27 (160.27), 28 (182.82), 29 (183.26). DEPT Technique (135 MHz, DMSO-$d_6$, $\delta$): 1 (111.15, 111.21), 2 (116.52, 116.58), 3 (118.97), 4 (124.05), 5 (124.13), 7 (126.83), 8 (126.98), 10 (131.94), 12 (132.25), 15 (134.26), 16 (135.06), 17 (135.23). Anal. Calcd for $C_{42}H_{24}O_4N_4 F_6$: C 66.14%, H 3.14%, N 7.34%. Found: C 66.07%, H 3.22%, N 7.32%.

## Polyamide Synthesis

The following general procedure, as illustrated in Scheme 2, was used for the preparation of PAs from diamine (5) and various dicarboxylic acids namely, 2,6-pyridine dicarboxylic acid, terephthalic acid, isophthalic acid, adipic acid, and sebacic acid. A typical polymerization reaction is as follows. BANQ (1.5 mmol), dicarboxylic acid (1.5 mmol), and LiCl (0.6 g) were dissolved in a mixture of pyridine (1 mL), triphenyl phosphite (1.2 mmol), and NMP (5 mL) in a 50-mL two-necked flask fitted with a mechanical stirrer. The resulting solution was stirred and heated at 110°C under argon for 18 h. The system was then cooled to room temperature and the solution was poured in 150 mL methanol to give a brown precipitate. The polymer obtained was filtered off and washed with hot water. All polymers were extracted in refluxing methanol to remove low molecular weight oligomers and then were vacuum-dried at 80°C.

## PA$_1$

This polymer was obtained from BANQ and terephthalic acid. Yield: 93% and $\eta_{inh}$ (dL/g): 0.62. FTIR (KBr, cm$^{-1}$): 3348 (NH amide stretching), 3035 (C—H aromatic stretching), 1691 (C=O amide stretching), 1604 (C=N stretching), 1525 (C=C stretching), 1222 (C—O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$ ppm): 10.65(2H, NH amide), 6.86-8.70 (24H, ArH). Anal. Calcd for $C_{50}H_{26}N_4O_6F_6$: C 67.26%, H 2.91%, N 6.28%. Found: C 67.21%, H 2.97%, N 6.25%.

## PA$_2$

This polymer was obtained from BANQ and isophthalic acid. Yield: 90% and $\eta_{inh}$ (dL/g): 0.53. FTIR (KBr, cm$^{-1}$): 3420 (NH amide stretching), 3035 (C—H aromatic stretching), 1671 (C=O amide stretching), 1605 (C=N stretching), 1504 (C=C stretching), 1221(C—O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$ ppm) : 10.76(2H, NH amide), 6.95-8.58(24H, ArH). Anal. Calcd for $C_{50}H_{26}N_4O_6F_6$: C 67.26%, H 2.91%, N 6.28%. Found: C 67.21%, H 2.97%, N 6.25%.

## PA$_3$

This polymer was obtained from BANQ and 2, 6-pyridine dicarboxylic acid. Yield: 87% and $\eta_{inh}$ (dL/g): 0.48. FTIR (KBr, cm$^{-1}$): 3422 (NH amide stretching), 3060 (C—H aromatic stretching), 1675 (C=O amide stretching), 1605(C=N stretching), 1508(C=C stretching), 1223(C—O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$ ppm): 10.27(2H, NH amide), 6.48-9.04(23H, ArH). Anal. Calcd for $C_{49}H_{25}N_5O_6F_6$: C 65.84%, H 2.80%, N 7.84%. Found: C 65.79%, H 2.87%, N 7.86%.

## PA$_4$

This polymer was obtained from BANQ and adipic acid. Yield: 85% and $\eta_{inh}$ (dL/g): 0.42. FTIR (KBr, cm$^{-1}$): 3423 (NH amide stretching), 3035(C—H aromatic stretching), 2933 (C—H aliphatic stretching), 1670 (C=O amide stretching), 1604 (C=N stretching), 1507 (C=C stretching), 1211(C—O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$ ppm): 10.26(2H, NH amide), 6.95-8.32 (20H, ArH), 2.17(4H, C—H aliphatic), 1.54(4H, C—H aliphatic). Anal. Calcd for $C_{48}H_{30}N_4O_6F_6$: C 66.05%, H 3.44%, N 6.42%. Found: C 65.95%, H 3.51%, N 6.45%.

## PA$_5$

This polymer was obtained from BANQ and sebacic acid. Yield: 84% and $\eta_{inh}$ (dL/g): 0.39. FTIR (KBr, cm$^{-1}$): 3425 (NH amide stretching), 3036 (C—H aromatic stretching), 2923 (C—H aliphatic stretching), 1669 (C=O amide stretching), 1604 (C=N stretching), 1507 (C=C stretching), 1217(C—O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$ ppm): 10.22(2H, NH amide), 6.99-8.32(20H, ArH), 2.16(4H, C—H aliphatic), 1.47(4H, C—H aliphatic), 1.26(8H, C—H aliphatic). Anal. Calcd for $C_{52}H_{38}N_4O_6F_6$: C 67.24%, H 4.09%, N 6.03%. Found: C 67.19%, H 4.15%, N 6.06%.

## Preparation of Electrode

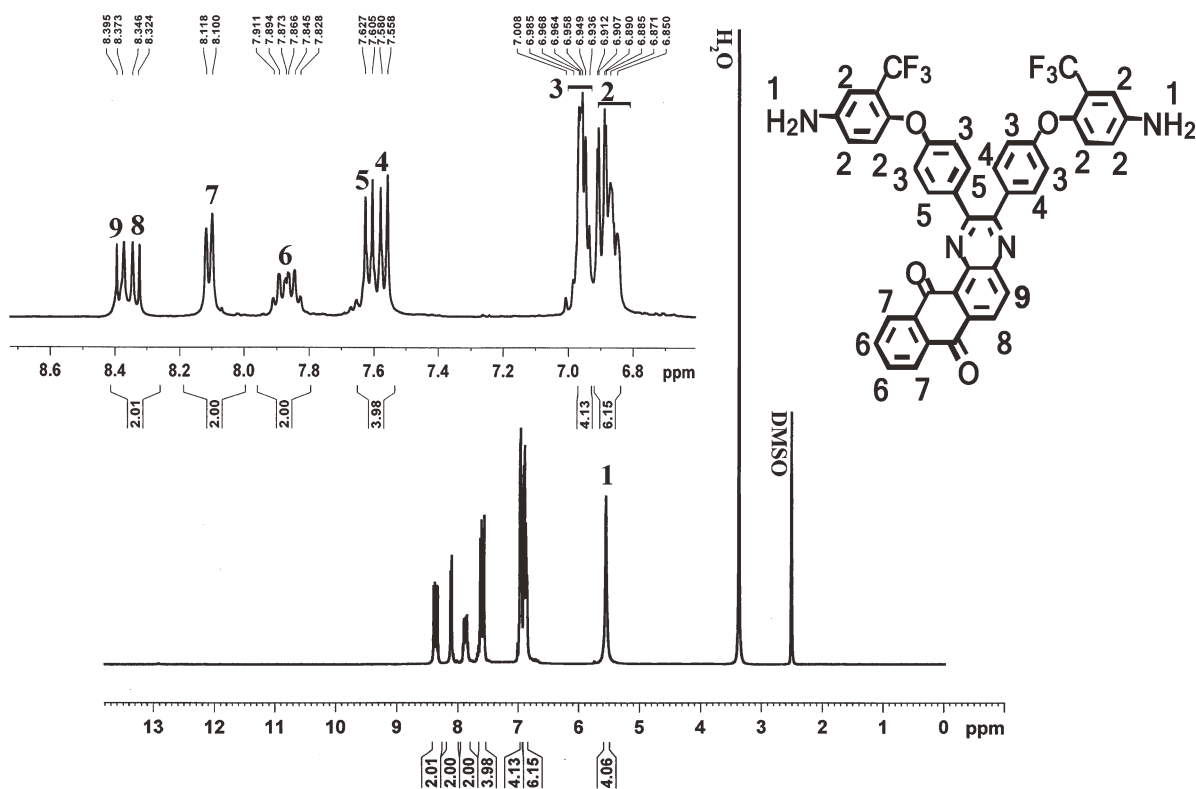The modified electrode was prepared according to the procedure given in the previous report.[28]

**Figure 1.** ^{1}H NMR spectrum of BANQ.

## RESULTS AND DISCUSSION

### Monomer Synthesis and Characterization

The synthesis of diamine (BANQ), 2,3-bis(4-(4-amino-2-(tri-fluoromethyl) phenoxy) phenyl)naphtho[2,3-f]quinoxaline-7,12-dione, was achieved according to the Scheme 1. Hydrolysis of 4,4′-dimethoxy benzyl in aqueous solution of HBr and glacial acetic acid was applied for the synthesis of 4,4′-dihydroxy benzyl. Addition reaction between an aromatic ortho-diamine and carbonyl groups of benzyl is a well known procedure for the preparation of quinoxaline system.[29,30] Thus 1,2-diaminoanthra-

quinone and 4,4′-dihydroxy benzyl in an addition reaction in acetic acid gave a bisphenol bearing aromatic functional of quinoxaline-anthraquinone in its structure, 2,3-bis(4-hydroxy-phenyl)naphtho[2,3-f]quinoxaline-7,12-dione (BNQ). The inter-mediate dinitro compound, 2,3-bis(4-(4-nitro-2-(trifluorome-thyl)phenoxy)phenyl)naphtho[2,3-f] quinoxaline-7,12-dione (BNNQ), was synthesized by aromatic nucleophilic displacement reaction between 2-chloro-5-nitrobenzotrifluoride and BNQ in the pres-ence of $K_2CO_3$ in DMAc at 110°C. The catalytic hydrogenation of the nitro groups in BNNQ compound gave the target



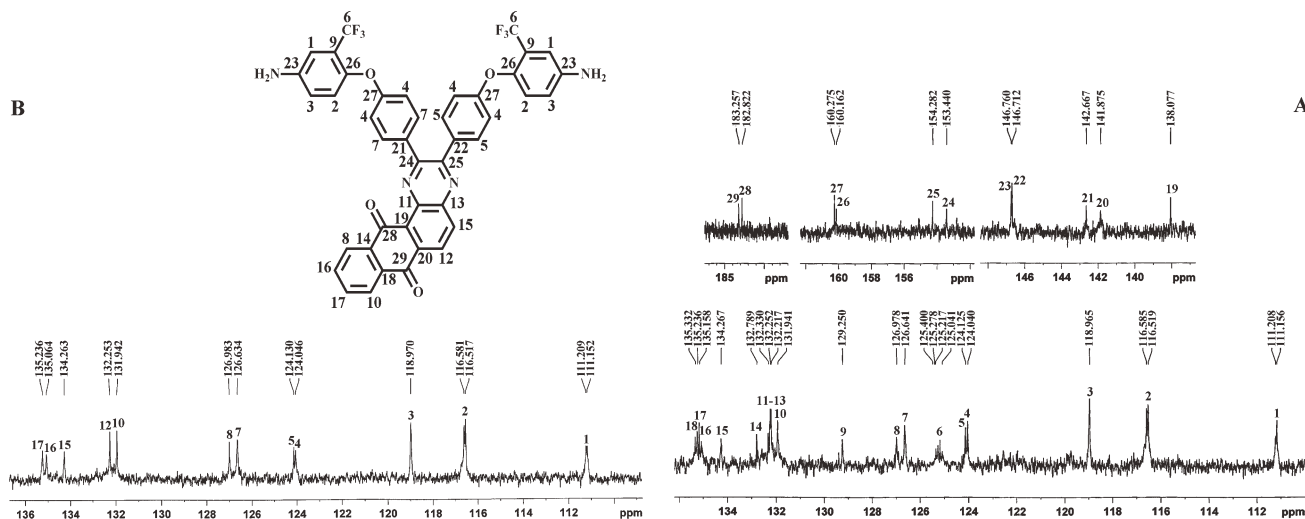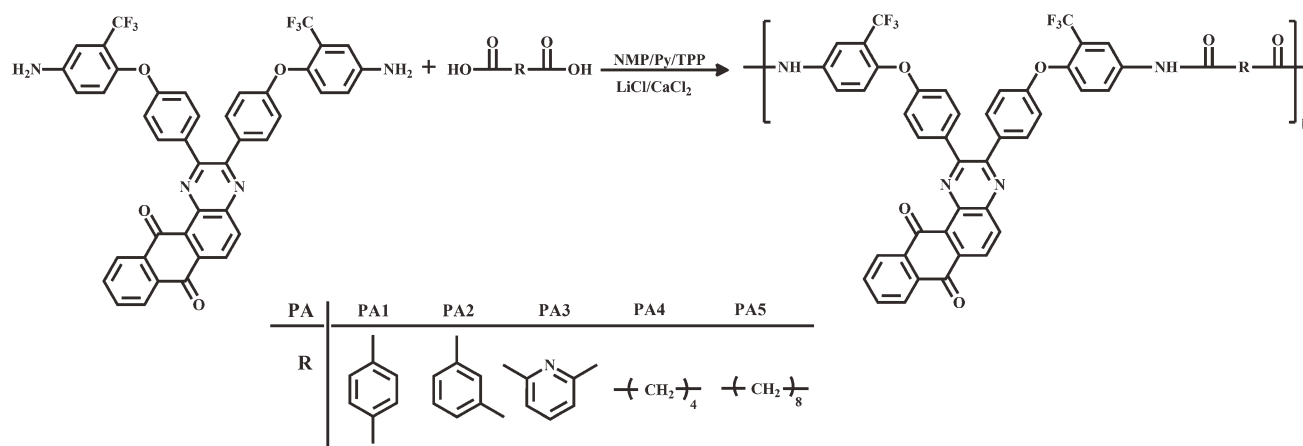**Figure 2.** ^{13}C NMR (A) and DEPT (B) spectra of BANQ.

**Scheme 2.** Synthetic procedure for preparation of PAs.

diamine, 2,3-bis(4-(4-amino-2-(trifluoromethyl)phenoxy)phenyl) naphtho[2,3-f]quinoxaline-7,12-dione (BANQ). The structure of intermediates and BANQ were characterized by using FTIR, $^1$H and $^{13}$C NMR spectroscopy (also DEPT technique), and elemental analysis, the extracted data were given in the experimental section. The FTIR spectrum of BNNQ showed absorption bands at 1536 and 1332 cm$^{-1}$ due to asymmetric and symmetric stretching vibrations of –NO$_2$ group while band at 1240 cm$^{-1}$ were assigned to C—O—C stretching vibrations. After reduction of BNNQ, the peaks at 1536 and 1332 cm$^{-1}$ disappeared and bands at 3384, 3274 cm$^{-1}$ due to N—H stretching were observed. The $^1$H NMR spectrum of BANQ, Figure 1, shows signals in the region of 5.55 and 6.85–8.38 ppm, related to the protons of amine group and aromatic ring, respectively. $^{13}$C NMR spectrum in Figure 2(A) and DEPT spectrum in Figure 2(B) of BANQ show the detailed description of the structure of this compound.

### Synthesis and Characterization of PAs
The objective of this study was the preparation of novel functionalized PAs of thermally stable and organosoluble in common solvents. As outlined in Scheme 2; aromatic and aliphatic PAs (PA$_1$ to PA$_5$) were synthesized by using direct polycondensation of diamine BANQ with various aromatic and aliphatic dicarboxylic acids such as 2, 6-pyridinedicarboxylic acid, terephthalic acid, isophthalic acid, adipic acid, and sebacic acid in NMP solution containing triphenylphosphite and pyridine as

catalyst. PAs had inherent viscosity in the range 0.39–0.62 dL/g at 30°C, indicating formation of medium molecular weight polymers. The average molecular weights of these PAs were not detected by GPC because of their very low solubility in THF eluent. The PAs were characterized by elemental analysis, and FTIR and $^1$H NMR spectroscopy. The FTIR spectra of the PAs exhibited the characteristic absorption bands at 3350 cm$^{-1}$ (N–H stretching), 1669–1691 cm$^{-1}$ (C=O stretching) and 1211–1223 cm$^{-1}$ (C—O stretching). The results of the elemental analyses were in good agreement with the calculated values of the proposed structures. In $^1$H NMR spectra of the PAs, signals at about 10.22–10.76 ppm were assigned to the N—H proton, and aromatic protons resonated in the region 6.86–8.70 ppm. The total protons in the spectra are consistent with the proposed chemical structure of the polymers.

### Solubility of PAs
The solubility behavior of these new aromatic PAs was determined at concentration of 5% (W/V) in a number of solvents and the results are tabulated in Table I. All PAs exhibited excellent solubility in polar aprotic solvents such as N-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and hexamethylphosphoramide (HMPA) at room temperature. The good solubility of these PAs was due to the fact that PAs containing bulky quinoxaline-anthraquinone and —CF$_3$ pendants exhibit a steric hindrance which prevents close chain-packing and allows the

**Table I.** Solubility Behavior and Viscosity of PAs

| PA code | $\eta_{inh}$ (dL/g)$^a$ | DMAc | DMF | NMP | DMSO | Py | THF | m-cresol | HMPA |
|---------|------|------|-----|-----|------|-----|-----|----------|------|
| PA$_1$ | 0.62 | ++ | ++ | ++ | ++ | + | − | + | ++ |
| PA$_2$ | 0.53 | ++ | ++ | ++ | ++ | + | − | + | ++ |
| PA$_3$ | 0.48 | ++ | ++ | ++ | ++ | ++ | − | + | ++ |
| PA$_4$ | 0.42 | ++ | ++ | ++ | ++ | ++ | + | ++ | ++ |
| PA$_5$ | 0.39 | ++ | ++ | ++ | ++ | ++ | + | ++ | ++ |

The solubility behavior of the PAs was determined at concentration of 5% (W/V).
(DMAc, N,N-dimethyl acetamide; DMF, N,N-dimethyl formamide; NMP, N-methyl pyrrolidone; DMSO, dimethyl sulfoxide; TCE, tetrachloroethan).
(++: Soluble at room temperature; + : Soluble on heating at 60°C; ± partially soluble on heating at 60°C; − Insoluble on heating at 60°C).
$^a$The inherent viscosity of the polymers was determined for the solutions of 0.5 g/dL in NMP at constant temperature of 25°C.
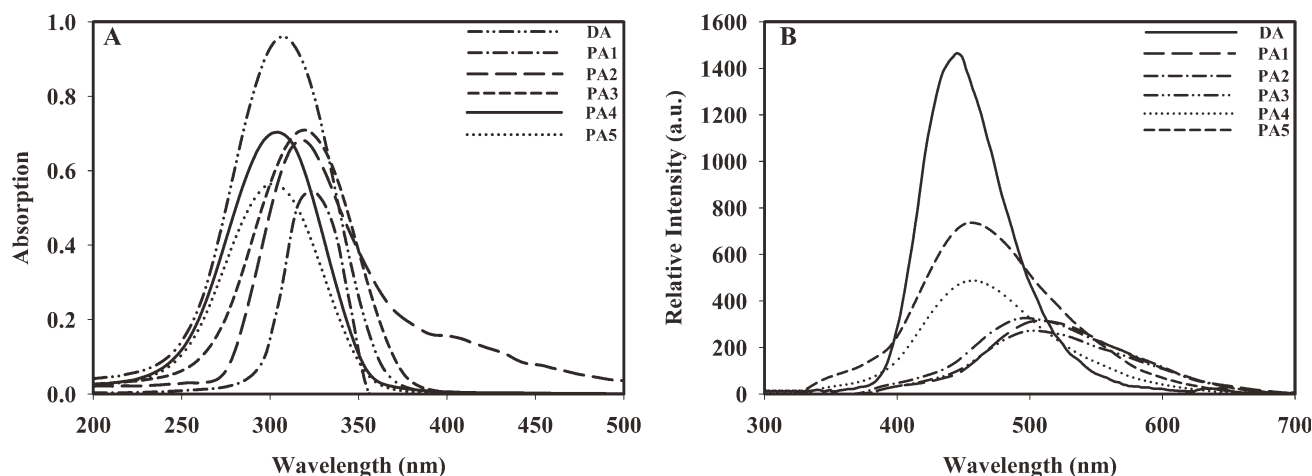
**Figure 3.** Absorption (A) and emission (B) spectra of diamine and PAs in NMP solution.

solvent molecules to diffuse into the polymer chains, and interact with polar groups in the polymer backbone. PA$_1$ and PA$_2$ dissolved in pyridine at 60°C, and PA$_4$ and PA$_5$ dissolved m-cresol at room temperature and in THF at 60°C. Although CF$_3$ groups increase solubility of the polymers but it reveals that two CF$_3$ groups in each repeating unit is not enough for the solubility of these PAs with bulky pendant of anthraquinone-quinoxaline. These PAs did not dissolve in lower polarity solvent of THF and for this reason the average molecular weight of these polymers were not detectable. In addition, the solubility varies to some extent depending upon the dicarboxylic acid used. PAs synthesized from aliphatic dicarboxylic acids (PA$_4$ and PA$_5$) exhibited better solubility behavior in comparison with aromatic PAs (PA$_1$ to PA$_3$) because of the presence of flexible methylene units in their backbone instead of rigid phenyl rings.

**Photophysical Properties of PAs**
The UV-vis absorption and photoluminescence spectra of the BANQ ($1.80 \times 10^{-5}$ M) and PAs in dilute (0.2 g/dL) NMP solution are shown in Figure 3 and for PAs in films (thickness 50 $\mu$m) are shown in Figure 4. As can be seen in these figures, the BANQ exhibited strong UV–vis absorption band with maxi-

mum at $\lambda_{\max(ab)}= 310$ nm and the PAs exhibited almost similar absorption peaks in solution and in solid state with maxima in the range 302–327 nm which can be related to the $\pi$ $\pi^\star$ transition of the conjugated aromatic systems of quinoxaline-anthraquinone.[31] To investigate the optical properties of thin films of these PAs, solutions of the polymers were made by dissolving about 0.50 g of the samples in 6 mL of NMP. These solutions were poured into a 5 cm glass Petri dish, which was heated under vacuum at 50°C for 1 h, 100°C for 2 h, and 150°C for 5 h to evaporate the solvent slowly. By being soaked in distilled water, the flexible and transparent thin films with almost no color was self-stripped off from the glass surface. The obtained films were then used to investigate the optical properties of the PAs. By comparing the absorption spectra, a slightly red shift is observed in the aromatic PAs spectra which can be due to expansion of $\pi$ system. The photoluminescence spectra were obtained by irradiative excitation at the wavelength of maximum absorption. The maximum emission of the BANQ in NMP solution ($1.80 \times 10^{-5}$ M), as shown in Figure 3(B), was observed at $\lambda_{\max(em)} = 450$ nm. As can be seen in Figures 3(B) and 4(B), the photoluminescence spectra of PAs in NMP solution (0.2 g/dL) and in films with about 50 $\mu$m thickness
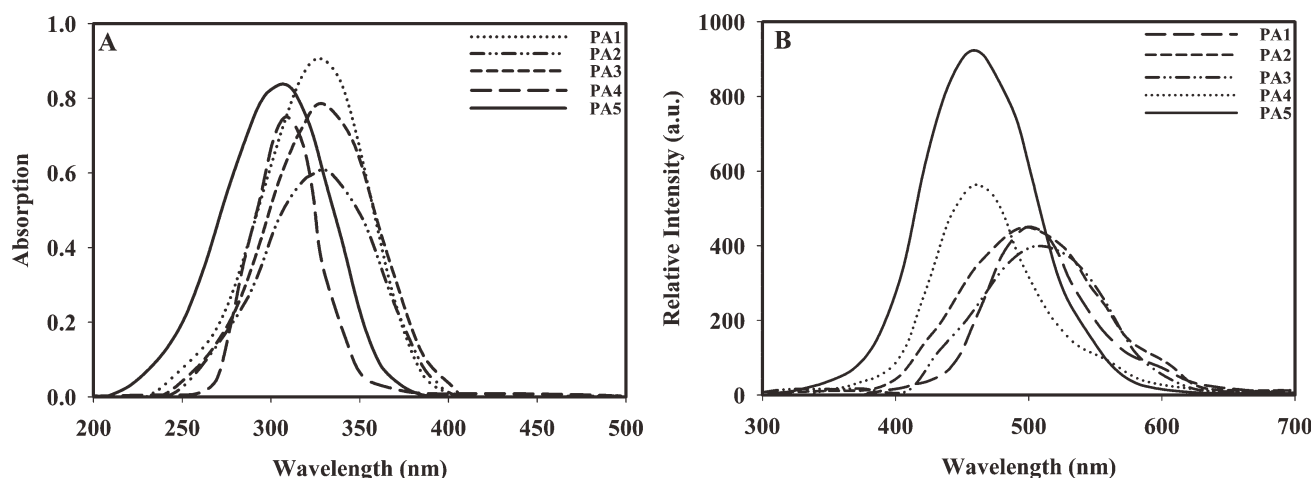


**Figure 4.** Absorption (A) and emission (B) spectra of PAs film.

**Table II.** UV-Vis Absorption and Photoluminescence Data of the Diamine and Pas

| Polymer | $\lambda_{abs}$ (nm)[a] | $\lambda_{em}$ (nm)[a] | $\lambda_{abs}$ (nm)[b] | $\lambda_{em}$ (nm)[b] | $\Phi_f$ (%)[c] |
|---------|------------|-----------|------------|-----------|-----------|
| DA | 303 | 449 | - | - | 27 |
| PA$_1$ | 327 | 507 | 327 | 501 | 8 |
| PA$_2$ | 324 | 497 | 326 | 499 | 6 |
| PA$_3$ | 324 | 502 | 327 | 508 | 7 |
| PA$_4$ | 304 | 457 | 309 | 462 | 12 |
| PA$_5$ | 302 | 451 | 305 | 459 | 17 |

Polymer concentration of 0.20 g/dL in NMP.
[b]UV-visible and fluorescence spectra of the PAs in solution (a) and film (b), respectively, [c]Fluorescence quantum yield relative to $10^{-5}$ M quinine sulfate in 1 N H$_2$SO$_4$ (aq) ($\Phi_{f = 0.55}$) as a standard.



**Figure 5.** DSC curves of PAs.

exhibited almost similar maxima around 490–510 nm in the green region for the aromatic PAs (PA$_1$, PA$_2$, PA$_3$) and around 450–460 nm for the aliphatic PAs (PA$_4$, PA$_5$). To measure the photoluminescence quantum yields ($\Phi_f$), dilute polymer solutions (0.2 g/dL) in NMP were prepared. A 0.1$N$ solution of quinine in H$_2$SO$_4$ ($\Phi_f = 0.55$) was used as reference according to the literature.[32,33] The $\Phi_f$ values measured at the maximum emission wavelength were 27% for the diamine (BANQ) at 450 nm, 12% and 17% for the aliphatic PAs at 460 nm, and 6–8% for the aromatic PAs at 500 nm. Table II lists some important optical data obtained from both these films and diluted solutions of the polymers in NMP. The blue shift and higher fluorescence quantum yield of the aliphatic PAs compared with the aromatic PAs could be attributed to reduced conjugation and capability of charge-transfer complex formation by the aliphatic diacids with the electron-donating diamine moiety in comparison to the stronger electron-accepting aromatic diacids.[15,34]
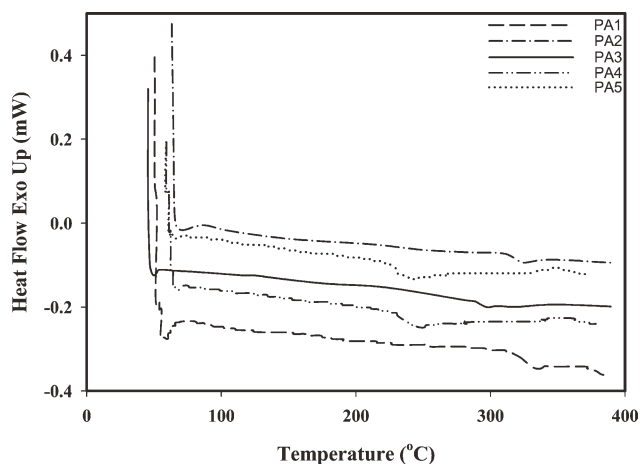
**Thermal Properties of PAs**
Thermal properties of these PAs were evaluated by DSC and TGA measurements with a heating rate of 10°C min$^{-1}$ under nitrogen, and the data extracted from the original curves were summarized in Table III. The absence of melting peak in DSC thermograms, Figure 5, supported the generally amorphous nature of the PAs. The glass-transition temperature values ($T_g$s) were determined from the midpoint temperature of base line shift were in the range of 230–323°C. Generally, polymers with bulky pendent groups lead to lower $T_g$s than polymers without bulky side groups owing to the greater interchain distance,

which lowers the force of the amide-amide hydrogen bonds that are to some extent responsible for the generally high $T_g$s of the aromatic polyamides. It is revealed that two factors affecting $T_g$ values of polymers are molecular packing state and chain rigidity. The increased rotational barrier caused by bulky aromatic pendent groups of diamine BANQ in these polymers and by additional —CF$_3$ substituents of diamine enhanced $T_g$ values. Therefore, the reason for the relatively high $T_g$s of these polyamides can be due to the high barrier for segmental mobility as a result of high-volume bulky pendant and side chain-side chain and side chain-main chain interactions. Also, as we expected, the $T_g$ values of these polymers showed dependence with the structure of the dicarboxylic acid component in the backbone. Therefore, the aromatic PAs (PA$_1$-PA$_3$) have higher $T_g$ than the aliphatic PAs. The ether linkage inserted in the main chains of these polymers lead to lowering of $T_g$ as well as significant improvement in solubility and processability.

Thermal stability of PAs was evaluated by TGA in nitrogen atmosphere at a heating rate of 10°C/min. The TGA curves are shown in Figure 6. There is less than 2% weight loss in the temperature range up to 250°C which can be mainly due to loss of

**Table III.** Thermal Characteristic Data of PAs

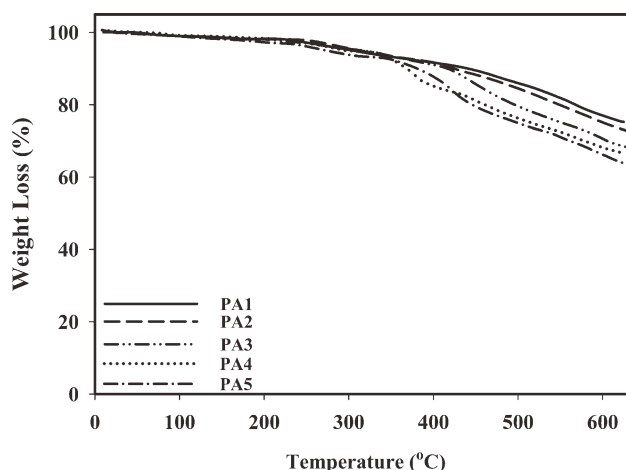| Polymer | $T_g$ (°C) | $T_{10}$ (°C) | C. Y. (%)[a] |
|---------|-----------|--------------|-------------|
| PA$_1$ | 323 | 415 | 76 |
| PA$_2$ | 320 | 410 | 72 |
| PA$_3$ | 295 | 404 | 69 |
| PA$_4$ | 238 | 360 | 67 |
| PA$_5$ | 230 | 362 | 65 |

$T_g$, glass transition temperature; $T_{10}$, temperature for 10% weight loss.
[a]C. Y.: Char yield: weight of residue at 600°C.



**Figure 6.** TGA curves of PAs.
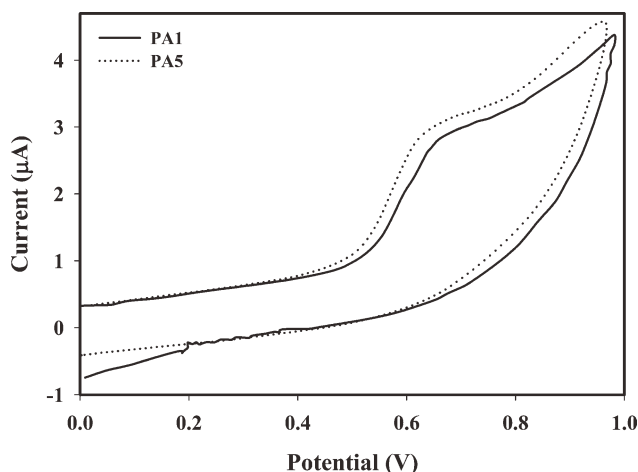
**Figure 7.** Cyclic voltammograms of $PA_1$ and $PA_5$ in CNTs paste electrode.

moisture trapped inside the polymer chains and was not removed during the initial drying process at 80°C. The temperatures of 10% weight loss ($T_{10}$) were taken in the range of 362–433°C. In addition, the amount of carbonized residue (char yield) for the resulting polyamides in nitrogen atmosphere was up to 76% at 650°C, implying that these polyamides possess good thermal stability. The high char yields of these polymers can be ascribed to their high aromatic content. The use of fluorinated monomers for modification of polymers is attractive due to the unique characteristics given by the presence of fluorine, such as outstanding chemical resistance, low coefficient of friction, low dielectric constant and water absorption, and thermal stability. The high thermal stability of these PAs can be due to rigid and bulky side group of quinoxaline-anthraquinone and also due to introduction of the electron negativity of $-CF_3$ groups with strong C—F bond that enhanced polarity of the polymer chain. The presence of different decomposition temperatures in TGA curves for each polymer can be due to presence of some molecular weight distribution. To compare thermal behavior, the aliphatic PAs have the lowest thermal stability with $T_{10}$ in the range of 362–372°C which is due to presence of flexible aliphatic units remained in the backbone from aliphatic dicarboxylic acids, in comparison with $T_{10}$ of 420–433°C of aromatic PAs with rigid phenyl groups remained from aromatic dicarboxylic acids.

**Electrochemical Properties**

We used the voltammetric method named cyclic voltammetry (CV) for the study of electrochemical behavior of one of these polymers at the surface of electrode modified with MWCNTs paste. The cyclic voltammograms were recorded with a scan rate of 100 mV s$^{-1}$.[28] The influence of nanocompound substance (CNT) on the oxidation of quinoxaline in an aqueous buffer solution (pH 7.0) was investigated. The voltammograms of $PA_1$ and $PA_5$ in Figure 7 showed similar anodic peaks at 0.64 V in forward scan which can probably be due to oxidation of quinoxaline group. The presence of CNTs in this polymer caused the electrical current to increase and the oxidation was observed. The backward scan showed no peak indicating that the oxidized product can not be reduced. This result shows that

these polymers are electrochemically oxidized at high potential and this process is not reversible.

## CONCLUSIONS

A series of high performance PAs were successfully obtained by direct polycondensation of aliphatic and aromatic dicarboxylic acids and a diamine containing several functionalities such as ether linkage, trifluoromethyl, quinoxaline, and anthraquinone groups. The prepared PAs exhibited much better solubility than commercial aramids because of the presence of these functional groups in the polymer backbone. These polymers also showed good thermal stability indicated by their high $T_g$ of 230–323°C and $T_{10}$ of 362–433°C. These polymers exhibited absorption in the far UV region and fluorescence emission in the visible region of 452–498 nm. Thus, photoactive organosoluble PAs with a combination of relatively high $T_g$s and thermal stability can be achieved by the incorporation of combined flexible and bulky functional groups in the main chains of the polymer.

## REFERENCES

1. Cassidy, P. E. Thermally Stable Polymer; Marcel Dekker: New York, **1980.**

2. Yang, H. H. Aromatic High-Strength Fibers; Wiley: New York, **1989.**

3. Oishi, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* **1988,** *21,* 547.

4. Chen, S.; Yin, Y.; Kita, H.; Okamoto, K. I. *J. Polym. Sci. Part A: Polym. Chem.* **2007,** *45,* 2797.

5. Tsuda, Y.; Kojima, M.; Matsuda, T.; Oh, J. M. *Polym. J.* **2008,** *40,* 354.

6. Wang, X. L.; Li, Y. F.; Zhang, S. J.; Ma, T.; Shao, Y.; Zhao, X. *Eur. Polym. J.* **2006,** *42,* 1229.

7. Liu, J. G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym. J.* **2007,** *39,* 543.

8. Shao, Y.; Li, Y.; Zhao, X.; Ma, T.; Gong, C.; Yang, F. *Eur. Polym. J.* **2007,** *43,* 4389.

9. Liaw, D.-J.; Liaw, B.-Y.; Yang, C.-M. *Macromolecules* **1999,** *32,* 7248.

10. Ghaemy, M.; Amini Nasab, S. M.; Alizadeh, R. *J. Appl. Polym. Sci.* **2010,** *116,* 3725.

11. Cheng, L.; Jian, X. G.; Mao, S. Z. *J. Polym. Sci. Part A: Polym. Chem.* **2002,** *40,* 3489.

12. Liaw, D.-J.; Liaw, B.-Y. *Polymer* **1999,** *40,* 3183.

13. Liaw, D.-J.; Chen, W.-H.; Hu, C.-K.; Lee, K.-R.; Lai, J.-Y. *Polymer* **2007,** *48,* 6571.

14. Liaw, D.-J.; Wang, K.-L.; Chang, F.-C. *Macromolecules* **2007,** *40,* 3568.

15. Ghaemy, M.; Amini Nasab, S. M. *React. Funct. Polym.* **2010,** *70,* 306.

16. Yen, H.-J.; Liou, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47,* 1584.

17. Espeso, J. F.; Ferrero, E.; de la Campa, J. G.; LozanoA. E.; de AbajoJ. *J. Polym. Sci. Part A: Polym. Chem.* **2001,** *39,* 475.

18. Ghaemy, M.; Barghamadi, M. *J. Appl. Polym. Sci.* **2009,** *114,* 3464.

19. Chen, S. H.; Shiau, C. S.; Tsai, L. R.; Chen, Y. *Polymer* **2006,** *47,* 8436.

20. Liaw, D. J.; Chen, W. H. *Polymer* **2003,** *44,* 3865.

21. Tundidor-Camba, A.; Terraza, C. A.; Tagle, L. H.; Coll, D. *J. Appl. Polym. Sci.* **2011,** *120,* 2381.

22. Ravikumar, L.; Kalaivani, S. S.; Murugesan, A.; Vidhyadevi, T.; Karthik, G.; Dinesh Kirupha, S.; Sivanesan, S. *J. Appl. Polym. Sci.* **2011,** *122,* 1634.

23. Karimi Zarchi, M. A.; Tayefi, M.; Tirgir, F.; SabzalianM. R. *J. Appl. Polym. Sci.* **2011,** *121,* 2818.

24. Yen, H. J.; Liou, G. S. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46,* 7354.

25. Zhou, H. G.; Liu, J. G.; Qian, Z. G.; Zhang, S. Y.; Yang, S. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2001,** *39,* 2404.

26. Yang, C. P.; Su, Y. Y.; Wen, S. J.; Hsiao, S. H. *Polymer* **2006,** *47,* 7021.

27. Wang, C. Y.; Li, P. H.; Li, G.; Jiang, J. M. *Colloid. Polym. Sci.* **2009,** *287,* 495.

28. Mallakpour, S.; Hatami, M.; Ensafi, A.; Karimi Maleh, H. *J. Sol. St Electrochem.* **2011,** *15,* 2053.

29. Ghaemy, M.; Porazizollahy, R.; Bazzar, M. *Macromol. Res.* **2011,** *19,* 528.

30. Ghaemy, M.; Hashemi Nasr, F. *J. Appl. Polym. Sci.* **2012,** *124,* 1707.

31. Liaw, D.-J.; Wang, K.-L.; Chang, F.-C. *Macromolecules* **2007,** *40,* 3568.

32. Feng, K.; Hsub, F. L.; Van DerVeer, D.; Bota, K.; Xiu, R. *J. Photochem. Photobiol. A:Chem.* **2004,** *165,* 223.

33. Liou, G.-S.; Hsiao, S.-H.; Chen, H.-W. *Mater. Chem.* **2006,** *16,* 1831.

34. Liou, G. S.; Chang, C. W. *Macromolecules* **2008,** *41,* 667.