

# Synthesis and characterization of new fluorescent polyimides bearing 1,2,4-triazole and 1,2-diaryl quinoxaline: Study properties and application to the extraction/elimination of metallic ions from aqueous media

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## ABSTRACT

In this article, synthesis and characterization of triazole-based polyimides for solid-phase extraction of metal cations is described. For this purpose, new aromatic diamines containing 1,2,4-triazole and substituted 1,2-diaryl quinoxaline units were synthesized and used in polycondensation reaction with aromatic dianhydrides to yield poly(triazole-imide)s (PTAI)s. These polymers had inherent viscosities in the range of 0.58–0.62 dL/g and were readily soluble in a variety of organic solvents; they formed low-colored and tough thin films via solution casting. The PTAIs exhibited  $T_g$  between 280 and 338 °C, and their 10% weight loss temperatures were in excess of 540 °C with up to 76% char yield at 700 °C in  $N_2$ . These polymers emitted green or blue fluorescence in dilute NMP solution and in the solid state. The triazole groups in the polymer chain were efficient chelating/host units for heavy metal ions. One of these polymers, PTAI(1b), was investigated for its extraction capability for environmentally deleterious metal ions such as  $Cr^{VI}$ ,  $Cr^{III}$ ,  $Co^{II}$ ,  $Zn^{II}$ ,  $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$  and  $Mn^{II}$  from aqueous solutions either individually or in the mixture and at different pH values.

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## 1. Introduction

Aromatic polyimides are versatile engineering polymers and have been applied widely in advanced technologies, due to their outstanding properties, such as excellent thermal and thermo-oxidative stabilities, chemical resistance, mechanical and electrical properties [1,2]. On the other hand, difficulty in processing these polymers due to their high softening temperature and poor solubility has led many researchers to incorporate different functional groups [3–5], including heterocycles [6–14], into the macromolecular chains to produce novel polyimides with improved processability without deteriorating their positive properties.

Various kinds of organic chelating resins including a variety of different polymer sorbents were synthesized and used for the extraction of metal ions [15–23]. Aromatic heterocyclic 1,2,4-triazole shows good electron affinity and hole-blocking property [24–27], and in this regard, the triazole derivatives are also well-known binding sites for the removal of metal cations from aqueous media, and the preparation of fluorescent on-off switchable chemosensors [28,29]. There is a great interest in triazole-based ligand which is primarily due to their stability under a variety of conditions and the fact that triazole ligands are mild Lewis bases and capable of

bonding with metal cations. Thus, the inclusion of the triazole heterocycle into macromolecular chains permits the preparation of polymers with good thermal and chemical properties that can be transformed into materials capable of interacting selectively with cations. Continuing with our line of research, new polyimides containing 1,2,4-triazole and substituted 2,3-diphenylquinoxaline functional groups in the main chain and lateral structure, respectively, were synthesized and characterized. The properties of the synthesized polyamides such as thermal, optical, water uptake, solubility, and their ability to remove environmentally toxic heavy metal ions such as  $Cr^{III}$ ,  $Co^{II}$ ,  $Zn^{II}$ ,  $Pb^{II}$ ,  $Cd^{II}$ ,  $Hg^{II}$ ,  $Mn^{II}$  and  $Cr^{VI}$  as  $Cr_2O_7^{2-}$  from aqueous media have been studied.

## 2. Experimental

### 2.1. Materials

All materials and solvents were purchased either from Merck or Fluka (Germany). Reagent-grade materials such as 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride (6FDA), pyromellitic dianhydride (PMDA), acetic anhydride, ethanol and methanol were used as received. N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and pyridine were purified by distillation over calcium hydride under reduced pressure and stored over 4 Å

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molecular sieves. Tetrahydrofuran (THF) and toluene were dried by sodium wire before use.

## 2.2. Synthesis of diamines

The diamines, as shown in Scheme 1, 4,4'-(4-(2,3-Diphenylquinoxalin-6-yl)-4H-1,2,4-triazole-3,5-diyl) dianiline (a), 4,4'-(4-(2,3-bis(4-methoxyphenyl)quinoxalin-6-yl)-4H-1,2,4-triazole-3,5-diyl) dianiline (b) and 4,4'-(4-(2,3-bis(4-bromophenyl)quinoxalin-6-yl)-4H-1,2,4-triazole-3,5-diyl)dianiline (c) were synthesized according to the procedures reported in the previous paper [30].

## 2.3. PTAI synthesis

The following conventional two-stage procedure, as illustrated in Scheme 1, was used for the preparation of all PTAs. A mixture of 1 mmol of a diamine [0.53 g(a) or 0.59 g(b) or 0.69 g(c)] and 10 mL dry NMP was stirred in a 250 mL three-necked round-bottomed flask at room temperature for 30 min. A 1 mmol of a dianhydride (0.21 g PMDA or 0.44 g 6FDA) was added and the mixture was stirred for 24 h to form a viscous solution of poly(amic acid) (PAA). The chemical imidization was carried out by stirring PAA solution with 3 mL of a mixture of acetic anhydride/pyridine (6/4, v/v) at 130 °C for 12 h to yield a homogeneous polymer solution, which was then poured slowly into ethanol to yield a precipitate that was collected by filtration. The precipitate was washed thoroughly with hot methanol and dried at 80 °C in a vacuum oven overnight. The yields after extraction of low molecular weight oligomers with hot methanol were in the range of 92–95%. The inherent viscosity of these polymers were in the range of 0.58–0.62 dL/g.

PTAI (1a): Yield = 95% and  $\eta_{inh} = 0.60$  dL/g. FT-IR (KBr): 3064 (C–H aromatic), 1780, 1721 (C=O imide), 1612 (C=N), 1483 (C=C), 1372 (C–N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.32\text{--}8.33$ (m, 23H) ppm.

PTAI (2a): Yield = 93% and  $\eta_{inh} = 0.62$  dL/g. FT-IR (KBr): 3036 (C–H aromatic), 1779, 1725 (C=O imide), 1604 (C=N), 1486 (C=C), 1373 (C–N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.32\text{--}8.46$  (m, 27H) ppm.

PTAI (1b): Yield = 94% and  $\eta_{inh} = 0.59$  dL/g. FT-IR (KBr): 3055(C–H aromatic), 1780, 1716 (C=O imide), 1603 (C=N),

1502(C=C), 1381 (C–N) and 1223 (C–O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 3.79\text{--}3.83$ (m, 6H) 7.12–8.46 (m, 21H) ppm.

PTAI (2b): Yield = 92% and  $\eta_{inh} = 0.61$  dL/g. FT-IR (KBr): 3054(C–H aromatic), 1781, 1718 (C=O imide), 1603 (C=N), 1502(C=C), 1381 (C–N) and 1226 (C–O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 3.80\text{--}3.85$ (m, 6H) 7.22–8.48 (m, 25H) ppm.

PTAI (1c): Yield = 95% and  $\eta_{inh} = 0.58$  dL/g. FT-IR (KBr): 3064 (C–H aromatic), 1781, 1720 (C=O imide), 1612 (C=N), 1483 (C=C), 1372 (C–N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.32\text{--}8.33$ (m, 21H) ppm.

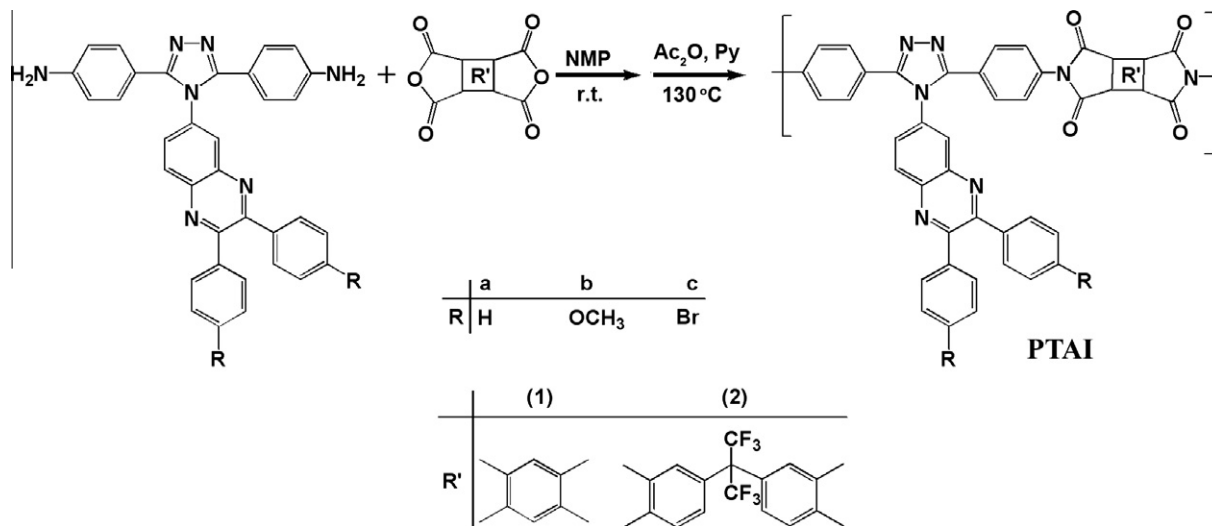
PTAI (2c): Yield = 93% and  $\eta_{inh} = 0.60$  dL/g. FT-IR (KBr): 3036 (C–H aromatic), 1779, 1725 (C=O imide), 1604 (C=N), 1486 (C=C), 1373 (C–N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.33\text{--}8.46$  (m, 25H) ppm.

## 2.4. Measurements

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer in the range of 4000–400  $\text{cm}^{-1}$ , using KBr pellets for solids.  $^1\text{H}$  NMR spectra were recorded on a 400 MHz Bruker Advance DRX spectrometer in DMSO- $d_6$ , using tetramethyl silane as an internal reference. Relative viscosity  $\eta_{rel}$  is determined by the ratio  $t/t_0$ . The inherent viscosity [ $(\eta_{inh})$ ] of PTAI was determined in NMP at 30 °C with an Ubbelohde suspended level viscometer. The solution concentration (C) is 0.5 g  $\text{dL}^{-1}$ . The inherent viscosity was calculated by using  $\eta_{inh} = \ln \eta_{rel}/C$  relationship. Polymer solubility was determined by stirring 5 mg polymer in 100 mL solvent at room temperature.

Thermogravimetric analysis (TGA) was conducted with TGA-50 analyzer in the temperature range of 30–700 °C at 10 °C/min under  $\text{N}_2$ . Differential scanning calorimetry (DSC) analysis was performed on a Perkin–Elmer Pyris 6 calorimeter at 10 °C/min under  $\text{N}_2$ . Glass transition temperatures ( $T_g$ )s were recorded at the middle of the transition in the heat capacity in the second heating scan after cooling from 350 °C.

UV-vis and fluorescence emission spectra were recorded in solution and in polymer films using a Cecil 5503 and Perkin–Elmer LS-3B spectrophotometers, respectively. To prepare crack-free and homogeneous thin films for the measurement of optical properties, solutions were made by dissolving about 0.5 g of PTAI in 5 mL DMF to afford an approximate 10 wt% solution. The homogeneous solution was poured into a 9 cm-diameter glass culture dish, heated



Scheme 1. Synthesis procedure for the preparation of PTAs.

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