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ORIGINAL ARTICLE

4-quinolin-8-yloxy Linked Triphenylamine Based Polyimides: Blue Light Emissive and Potential Hole-Transport Materials

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Abstract A series of fluorescent donor- acceptor (D-A) alternating copolyimides (P1, P2, P3 and P4) with 4-quinolin-8-yloxy linked triphenylamine main polymer chain have been synthesized by conventional polycondensation. All the synthesized co-polyimides were characterized by elemental, gel permeation chromatography and FTIR spectral analysis. These newly prepared PIs possess HOMO energy levels in range of -4.74 to -4.78 eV and have medium optical band gaps. The photoluminescence spectral analysis revealed blue to violet emission with appreciable efficiency with lower onset oxidation potentials suitable for the facile hole injection materials. All the photophysical and electrochemical properties were also explored in context of effect of the pendant 4- quinolin-8-yloxy, indicating suitable combination of donor (TPA) on one hand and imide and pendant as acceptor on both ends.

Keywords Copolyimides · 4-quinolin-8-yloxy · Fluorescent · Triphenylamine · Blue emission · Hole injection materials

Introduction

Polyimides are recognized as an important class of high-performance polymers for their exceptionally good thermo-oxidative, mechanical, and electrical properties [1]. Thus, polyimides have been widely explored for applications in numerous fields like adhesives, automobiles, fuel cells, and aerospace [2, 3]. Instead of this versatility in properties, aromatic polyimides tend to show less solution processability owing to the interchain interactions and rigidity of polymeric chains which restrict their utility. Hence, now a days different aspects of the structural variation among monomers and their polymers are being explored to establish the structure property relationship [4–6].

Triphenylamine (TPA) based polymeric materials are widely designed and explored for solar cells, electrochromic devices, and OLEDs applications [7–9]. Possession of propeller shape, anodic oxidation, and radical cation formation at lower oxidation potentials make TPA moiety a suitable candidate for optoelectronic applications [10–12]. The stability of the radical cation formed after the oxidation of the TPA unit plays a key role in the application of TPA-based polymers in optoelectronic properties. It is well established that the electronic strength of the substitution (electron-donating or electron-withdrawing nature) affects the electrochemical properties of materials containing the TPA moiety. Electron-donating substituents, mainly at the para orientation of TPA unit, prevent the coupling reactions and enhance the stability of radical cations [13–15]. However, few studies have shown that electron withdrawing substituents also present interesting properties. In view of this, TPA-based polymers with electron-withdrawing groups (such as quinoxaline, CN, CF_3 and NO_2) have already been reported and considered as promising candidates for opto-electrical applications [16–18]. These polymers exhibited

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blue emission, adjustable band gaps with electrochemical stability, high hole mobility and high electrochromic contrast. Therefore, numerous attempts have been made for the design and synthesis of new TPA based diamines and dianhydrides comprising both electron donating and electron withdrawing groups in order to tailor the properties of resulting polymers. Moreover, the incorporation of flexible ether linkages in polymers is of particular interest as ether linkages disrupt the linear progression of the polymeric spine and also affords lower internal energy of rotation [19]. Thus, the polyimides with ether linkages are known to have enhanced melt processability, lower dielectric constant and good optical transparency.

In our previously reported work TPA based electroactive polyimides with naphthoxy pendant group displayed potential optical and electrochemical properties suitable for electrochromic applications, based on that work we intended to investigate the effect of electron withdrawing pendant group (nitrogen analogue of naphthoxy group) [20].

We synthesized the diamine N^1-(4-aminophenyl)-N^1-(4-(quinolin-8-yloxy) phenyl) benzene-1,4-diamine containing 4-quinoline-8-yloxy as a pendant group in triphenylamine unit recently reported by Wanan et al. [21] This diamine was reacted with 4 different dianhydrides to prepare polyimides. Through in depth photophysical and electrochemical studies it was found that the synthesized polyimides have properties which are desirable for optoelectronic applications like lower onset oxidation potential, high lying HOMO coupled with good solubility in organic solvents, and good film forming ability.

Experimental

Materials and Methods

4-Fluoro-1-nitrobenzene, 8-hydroxyquinoline, 4,4′-oxydianiline, pyromellitic dianhydride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, 4,4′-oxydiphthalic anhydride (ODPA), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, *N,N′*- dimethylformamide (DMF) tetrahydrofuran (THF) and *N,N′*-dimethylacetamide (DMAc) were purchased from Aldrich and used as received. Gallenkamp with digital thermometer (Sanyo MPDBM 3.5) was used to determine the melting points of intermediates and final compounds. Bruker α-Alpha-P model was employed to record FTIR- spectra using ATR method. A Bruker AM (300 MH) spectrophotometer was used to collect ^{1}H-NMR and ^{13}C-NMR spectra in hexadueterodimethylsulfoxide (DMSO-d$_6$) solution, and TMS was taken as internal standard reference. CHNS analyzer Cary, 100 Conc UV–visible spectrophotometer and PC1-Photon counting spectrofluorometer were used to record UV–visible spectra and fluorescence spectra. High-temperature (GPC) instrument calibrated with various standards of polystyrene (model PL-GPC 220), a refractive-index detector and 0.1% LiBr as an eluent was used to determine the molecular weight distribution in the terms of the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the PIs. Electrochemical behavior was studied by cyclic voltammetry; polyimides were spin coated on ITO glass substrates, as working electrode. The electrochemical analyzer (BAS-100 B) was used with 0.1 M $LiClO_4$ as supporting electrolyte in anhydrous acetonitrile versus reference (Ag/AgCl) and platinum wire as counter electrode under nitrogen atmosphere.

Monomer Synthesis

4-Nitro-N-(4-nitrophenyl)-N-(4-(quinolin-8-yloxy)phenyl) benzenamine (3) was prepared by reacting 4-flouro-1-nitrobenzene (21.22 mmol) and cesium fluoride (22.22 mmol) in DMSO (20 mL) with the solution of 4-(8-quinolinoxy) aniline (0.23 g, 10 mmol) in DMSO (10 mL). The reaction mixture was heated at 120 °C for 24 h and reaction progress as monitored by thin layer chromatography. After completion of the reaction, the mixture was precipitated in 250 ml ice-cooled water, filtered off and purified by recrystallization in absolute ethanol as yellow solid. Yield: 89%. M.p: 189 °C, $R_f = 0.61$ (*n*-Hexane: EtOAc,3:1) FT-IR (ῡ/cm^{-1}): 1344 (C-N ter amine stretch), 1583, 1472 (-NO_2 stretch); ^{1}H NMR (300 MHz, DMSO-*d6*), 8.17(m,4H, Ph-H 2,2′), 7.24 (m, 4H, Ph-H, 3,3′), 7.01 (m, 5H, Ph-H 7,7′,10,11,12), 6.8(m, 6H, Ph-H 6,6′),8.31(m, 1H, Ph-H, 14), 7.67(m, 1H, Ph-H,15),8.9 (m, 1H, Ph-H,16).^{13}C NMR δ (ppm)149 (1), 114 (2,2′), 124 (3,3′), 140 (4), 145 (5), 128.9 (6,6′), 122.3 (7,7′), 152.1 (8), 154.09 (9), 121.6 (10), 122.5 (11), 123.2 (12), 126.8 (13), 135.8 (14), 114.3 (15), 149.9 (16), 138.8 (17). Anal for $C_{27}H_{18}N_4O_5$ (%).Calcd. C = 67.78, H = 3.79, N = 11.71, Found C = 67.80, H = 3.75, N = 11.74.

Synthesis of N^1-(4-Aminophenyl)-N^1-(4-(quinolin-8-yloxy) phenyl)benzene-1,4-diamine (4)

For the synthesis of 4-Nitro-N-(4-nitrophenyl)-N-(4-(quinolin-8 yloxy)phenyl)benzenamine (4) reduction of (3) was carried out by reacting compound (3) (2.0 g, 4 mmol), 10% Pd/C (0.2 g), and ethanol (50 mL) in a 250 mL three neck round bottom flask. Afterwards, to this boiling solution/suspension hydrazine monohydrate (7 mL) was added dropwise. The reflux was continued for 24 h, monitored by TLC and after complete reduction, Pd/C was hot filtered from the solution, filtrate was concentrated to collect solid product by filtration. The crude product was purified by recrystallization in ethanol as light yellow solid. Yield: 68%. M.p. 232 °C, $R_f = 0.34$ (*n*-Hexane: EtOAc,1:1), FTIR ῡ (cm^{-1}):

(3439, 3335 -NH_2 stretch), (1359 C-N stretch of tertiary amine), ^{1}H NMR (300 MHz, DMSO, TMS 25 °C) δ (ppm) 6.52(d $J=8.4$ Hz, 4H, Ph-H 2,2′), 6.87(m,4H,Ph-H,3,3′), 6.68 (d, $J=9$, 2H,Ph-H 6,6′), 6.8(m,2H,Ph-H 7,7′), 7.09 (m, 1H, Ph-H 10), 7.47 (m,1H,Ph-H, 11), 7.52 (m,1H,Ph-H,12), 8.39 (m,1H,Ph-H,14), 7.65(m,1H,Ph-H,15), 8.8 (m,1H,Ph-H,16), 4.95 (NH_2,s, 4H).^{13}C NMR δ (ppm) 145 (1), 115 (2,2′), 127(3,3′), 136(4), 146 (5), 129 (6,6′), 122 (7,7′), 150 (8), 154 (9), 122.6 (10), 122.5 (11), 123 (12), 127 (13), 136 (14), 115 (15), 149 (16), 140 (17) Anal for $C_{27}H_{22}N_4O$ (%): Calcd C = 77.49, H = 5.30, N = 13.39, Found C = 77.51, H = 5.28, N = 13.41 (Fig. 1).

Synthesis of Polyimides (P1-P4)

Commercially available four carboxylic dianhydrides including PMDA, BTDA, 6FDA, and ODPA were reacted with 4-quinoline-8-yloxy based diamine monomer (**4**) and a series of novel polyimides was prepared (Fig. 2). To an amount of 0.001 mol of DA (**4**) and 0.001 mol of ODA, 6 mL of anhydrous DMAc was added in a vacuum-packed glove box under anhydrous condition. Afterwards, to this clear solution a calculated amount of dianhydride was introduced in one portion. The reaction mixture became viscous with the initiation of polymerization, making stirring difficult. To facile stirring, additional amount of DMAc was added to the reaction mixture keeping solid contents of polymer solution to 12 wt %. After 6 h of stirring, a slight excess of dianhydride was added, in order to confirm anhydride as chain-end groups and recompense for any lost anhydride functional groups. The reaction mixture was transformed into highly viscous poly(amic acid) (PAA) solution after 18 h continuous stirring under inert and anhydrous conditions. PAA films were cast by solvent evaporation technique by heating the solution at 70 °C for 12 h. Subsequently, PAA films were heated successively at 100, 200, and 300 °C for 1 h each and flexible free standing polyimide films were obtained.

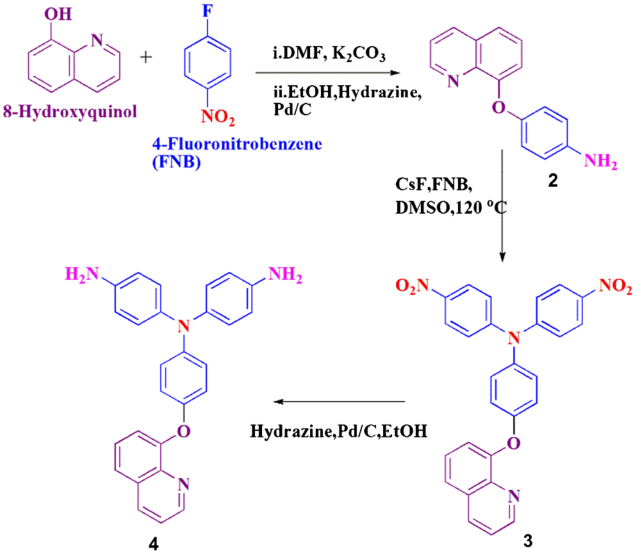


Fig. 1 Synthesis of N^1-(4-aminophenyl)-N^1-(4-(quinolin-8-yloxy)phenyl)benzene-1,4-diamine (**4**)

P1 ANAL Calcd. for $C_{49}H_{32}N_6O_6$, $C=73.46$, $H=3.96$, $N=10.60$ and found to be $C=73.49$, $H=4.03$, $N=10.49$. FTIR: (ῡ/cm^{-1}) 1782 (asymmetric C=O stretching imide), 1723(symmetric C=O stretching, imide), 1360 (C-N, TPA), 720 (imide ring deformation).

P2 ANAL Calcd. for $C_{56}H_{36}N_6O_7$, $C=73.98$, $H=4.06$, $N=9.41$ and found to be $C=73.94$, $H=3.98$, $N=9.49$. FTIR: (ῡ/cm^{-1}) 1776 (asymmetric C=O stretching imide), 1719(symmetric C=O stretching, imide), 1372 (C-N, TPA), 715 (imide ring deformation).

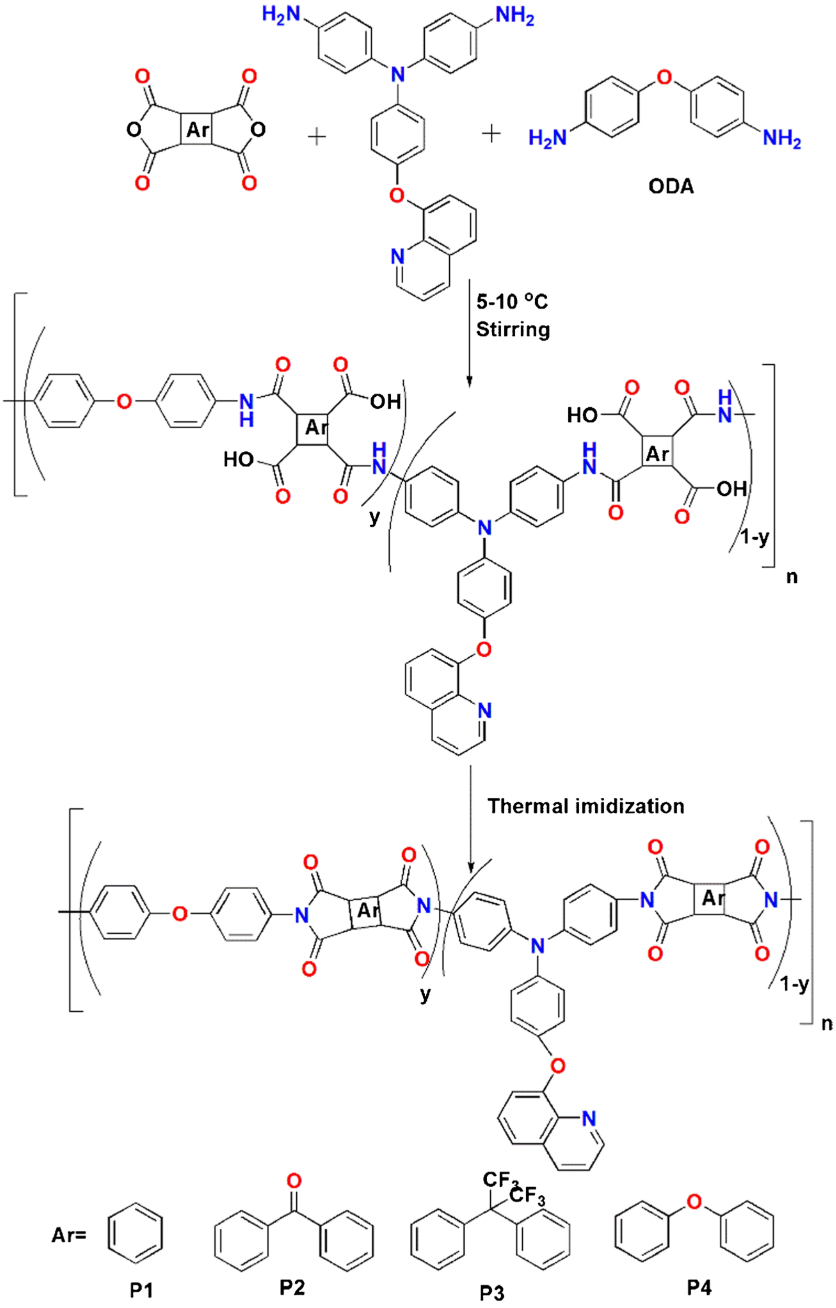
P3 ANAL Calcd. for $C_{58}H_{36}F_6N_6O_6$, $C=67.84$, $H=3.53$, $N=8.18$ and found to be $C=67.8$, $H=4.01$, $N=8.21$. FTIR: (ῡ/cm^{-1}) 1772 (asymmetric C=O stretching imide),1728 (symmetric C=O stretching, imide), 1369(C-N, TPA), 725 (imide ring deformation).

P4 ANAL Calcd. for $C_{55}H_{36}N_6O_7$, $C=73.98$, $H=4.06$, $N=9.41$ and found to be $C=73.96$, $H=3.97$, $N=9.52$. FTIR: (ῡ/cm^{-1}) 1780 (asymmetric C=O stretching imide), 1708 (symmetric C=O stretching, imide), 1367 (C-N, TPA), 712 (imide ring deformation).

Results and Discussion

The diamine monomer N^1-(4-aminophenyl)-N^1-(4-(quinolin-8-yloxy)phenyl)benzene-1, 4-diamine was synthesized in four steps, as presented in Fig. 1. In first step (**1**) was prepared according to the method reported by Wanan et al. by reaction of 8-hydroxy quinoline with 4-fluoronitrobenzene in the presence of potassium carbonate, and then (**1**) was catalytically reduced to (**2**) in the presence of Pd/C and hydrazine in ethanol and good yield was observed. In the third step, (**2**) was subjected to cesium fluoride facilitated nucleophilic N-arylation with 4-fluoronitrobenzene and TPA based dinitro compound (3) was achieved which on reduction yielded TPA based diamine (4) in a good yield [21]. The completion of synthesis and targeted structure of diamine and its dinitro precursor were evaluated by elemental and spectroscopic methods. In FTIR spectrum of dinitro precursor (**3**), the characteristic absorption peaks of nitro groups were observed at 1530 and 1340 cm^{-1} [22] which on reduction disappeared and two most significant absorption peaks at 3450 and 3360 cm^{-1} for –NH_2 appeared as shown

Fig. 2 Synthesis of polyimides



in Fig. 3. Moreover a characteristic absorption band for C-N (ter. amine) was observed at 1367 cm^{-1} whereas, another absorption band at around 820 cm^{-1} confirmed the *para* substitution pattern of the diamine monomer (**4**).

In the ^{1}HNMR spectrum of (**3**), a deshielded doublet observed at 8.3 ppm was assigned to the protons ortho to the nitro groups. After reduction of compound (**3**) to (**4**), the resonance signal for protons ortho to amino shifted up field at 6.52 ppm values suggesting the change in functionality. In addition, a singlet corresponding to the amino proton at 4.8 ppm was observed which confirmed the successful confirmation of formation of 4. Moreover the up field signals from 6.68 to 6.8 ppm were attributed to the protons which are ortho to TPA linkage due to the electron donating nature of TPA linkage whereas rest of the signals of 4-(quinoline-8-yloxy) moiety were in well accordance with the reported data [23].

The ^{13}C NMR spectra of (**3**) and (**4**) also confirmed the proposed triphenylamine based dinitro and diamine structures. In the ^{13}C NMR of (**3**) the signal at 149 ppm was assigned to ipso carbon bearing nitro group and after the reduction of (**3**) into 4 the ipso carbon bearing amino was shifted up field at ppm 145 as presented in Fig. 4. Further by elemental analysis the experimentally determined

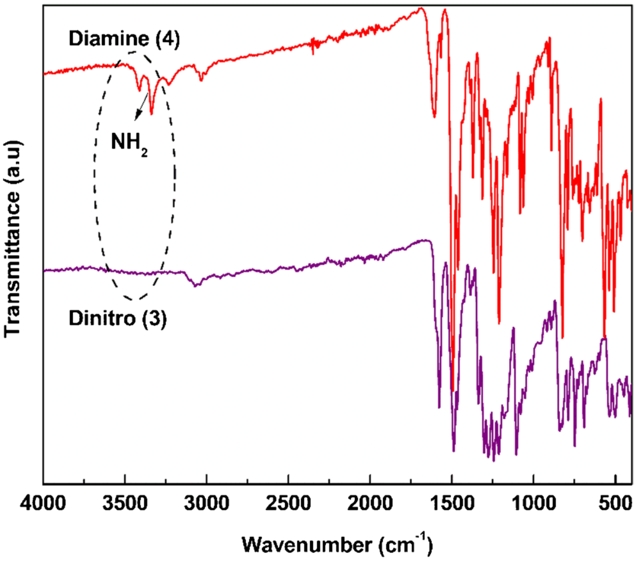


Fig. 3 FT-IR spectra of DN (3) and DA (4)

percentages were found to be in good agreement with calculated values for (**3**) and (**4**) which confirmed their proposed structures.

Polyimide Synthesis

The newly synthesized 4-quinoline-8-yloxy and triphenylamine based diamine monomer **(4)** was polymerized with few selected aromatic dianhydrides (PMDA, BTDA, 6FDA, and ODPA) in a stoichiometric amount, following two step conventional imidization method in order to study the effect of rigidity and flexibility in the targeted polyimide chains. In the first step, high molecular weight poly(amic acids) PAAs were prepared and a small portion of PAAs was spin coated on ITO glass substrate and rest of the material was placed in petri dishes. These PAAs (both the spin coated and in petri dishes) were thermally imidized into respective polyimides PIs in the second step. The complete conversion of PAA into PI was examined by the FTIR spectroscopy and the FTIR spectra of PIs P1-P4 are presented in Fig. 5. It is apparent that, absorption band at 1650 cm^{-1} diagnostic absorption band of C=O of amide of PAA, was disappeared in the FTIR spectra of PIs, approving the complete transformation of PAA into PI. Additionally, the arrival of new absorption bands, in the spectra of PIs, at 1770 cm^{-1} (asymmetric C=O stretching), 1708 cm^{-1} (symmetric C=O stretching), 1370 cm^{-1} (symmetric C–N stretching), and 719 cm^{-1} (imide ring deformation) additionally confirmed complete imidization of PAA into PI. Moreover, the observed elemental analysis proved the successful synthesis of polyimides from diamine 4. As the polyimides were not completely soluble in deuterated solvents available for NMR due to which NMR spectral analysis could not carried out.

The elemental analysis also showed the good agreement between the calculated percentages of carbon, hydrogen and nitrogen and observed values which validated the successful polyimide synthesis.

Viscosity and Molecular Weight Analysis of PIs P1-P4

The synthesized polyimides P1-P4, were dissolved in NMP to estimate their inherent viscosities, as enlisted in Table 1, inherent viscosities varied from 0.92 to 1.18 dL/g. The results demonstrated that the P1 and P2 showed the higher η_{inh} attributed to the rigid units hence attained better packing efficiency. In P3, the suppression of the chain packing was owed to the presence of voluminous hexafluoroisopropylidene group hence lower η_{inh} value was displayed [24]. These results were further supported by the number and weight-average molecular weight (M_n, M_w) and the polydispersity index determined by the GPC as enlisted in Table 1. M_n and M_w of the PIs P1- P4 were found in the range of 41,650 – 51,991 and 67,472 – 81,106 g/mol respectively, with polydispersity index in the range of 1.51–1.64. The M_n, M_w of naphthalene based polyimides were ranged between 38,197–45,251 and 64,935–75,775 g/mol respectively which were comparatively lower than these newly prepared 4-quinolin-8-yloxy and TPA based polyimides. This signifies the accomplishment of reasonably high molecular weight by synthesized polyimides and 4-quinolin-8-yloxy derived TPA based diamine monomer (**4**) has better polymerization activity than the analogous naphthalene based diamine monomer [20].

Organo Solubility of PIs P1-P4

The organo solubility of all the prepared PIs (P1-P4) was determined in different organic solvents by preparing 1% W/V solution using 10 mg of the polymer sample in 1 mL of solvent at different temperatures and solubility data is summed up in Table 2. It was obvious from the results that the chemical structure of polyimide greatly affects the solubility in different solvents. The PIs displayed good solubility in polar aprotic solvents like DMSO, DMAc and NMP at heating and even in less polar solvent such as *m*-cresol. This may be manifestation of ether linkage between TPA and 4-quinolin-8-yloxy moiety which reduces the symmetry among the polymeric chains hence disrupting the chain packing.

Among all PIs, P1 and P2 showed comparatively lower solubility with rest of the members owing to the rigidity and dense chain packing of polymer chains. While, in P3 the bulky hexafluoroisoprpylidene groups could cause low molecular packing due to presence of rotatable –CF$_3$ groups hence better solubility [25]. These polyimides displayed comparable solubility with the naphthalene-TPA based

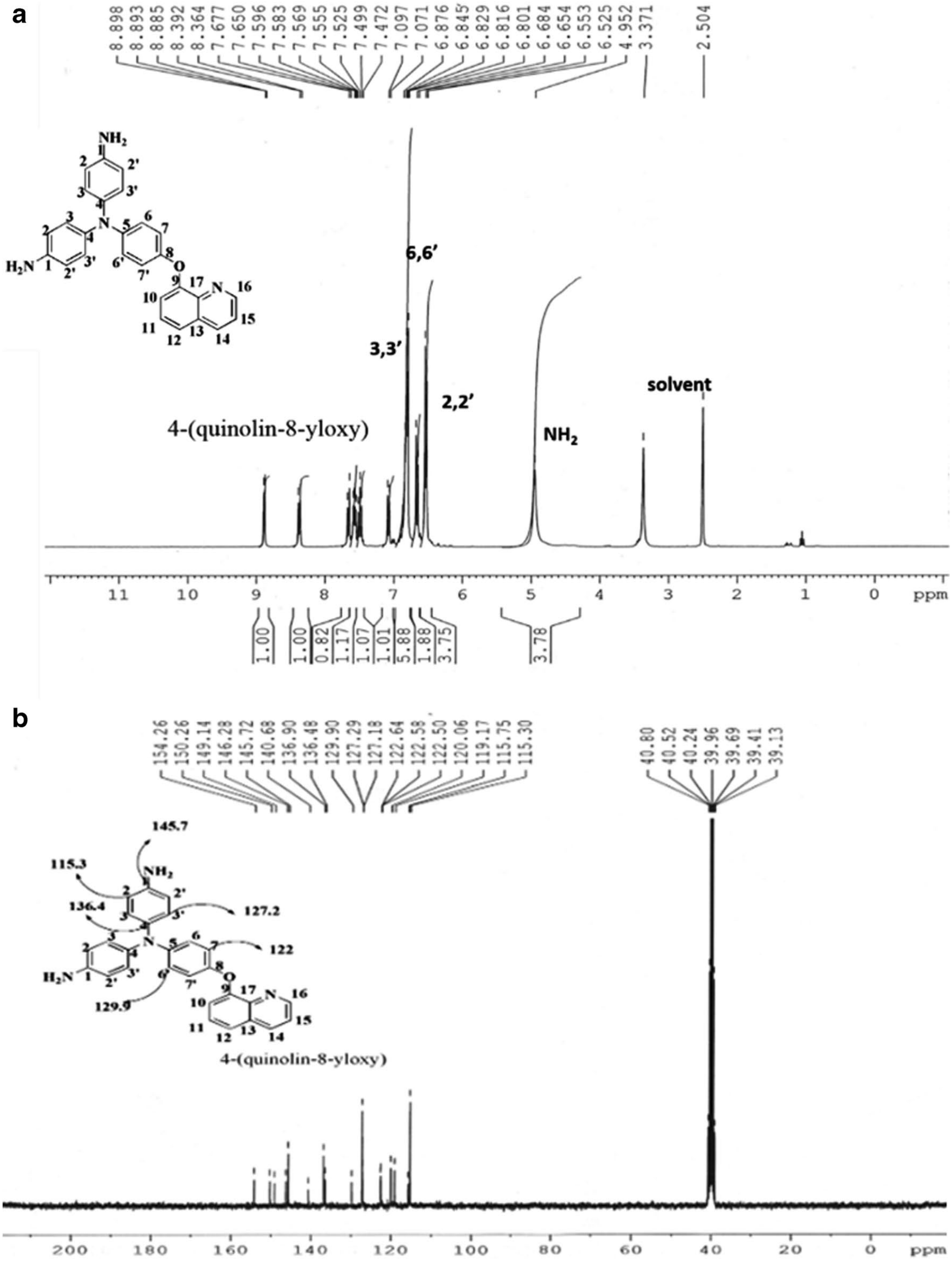


Fig. 4 **a** ^{1}H NMR spectrum of 4. **b** ^{13}C NMR spectrum of 4

polyimides, however, an improved solubility in general was observed when compared to the polyimides without TPA, polyimides with simple TPA unit, and with *ter*-butyl pendant group reported earlier.

Photophysical Properties of PIs P1-P4

To get an insight of the optical properties of our synthesized polyimides, absorption and emission studies were

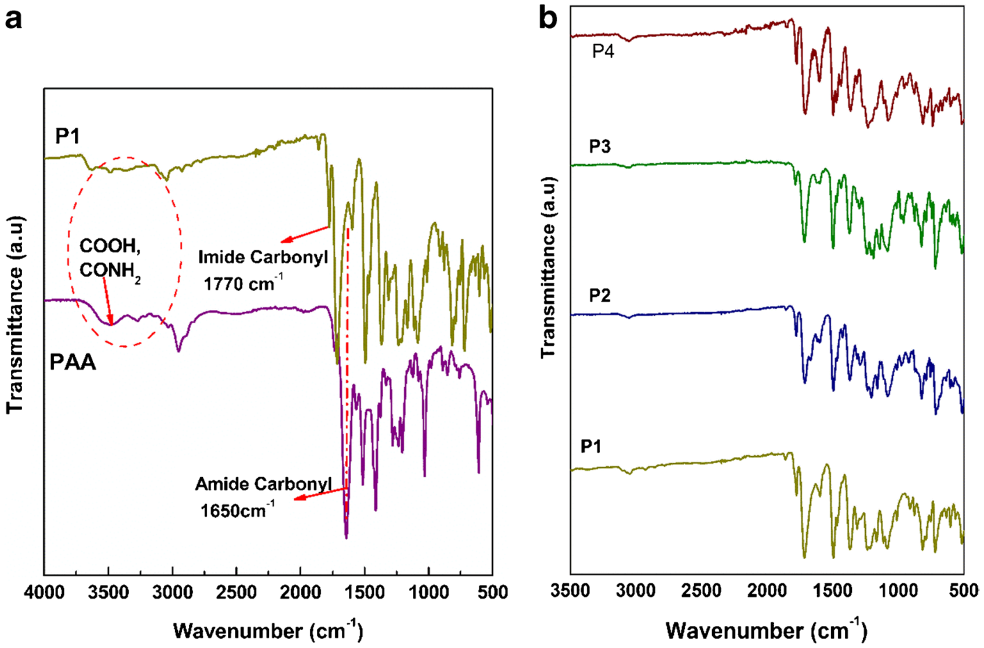


Fig. 5 **a** FTIR spectra of polyamic acid (PAA) and polyimide P1. **b** FTIR spectra of PIs P1-P4

Table 1 GPC data of PIs P1-P4

Codes	η dL/g	M_w g/mol	M_n g/mol	PDI
P1	1.15	81,106	51,991	1.56
P2	1.18	75,482	49,988	1.51
P3	0.92	67,472	41,650	1.62
P4	0.96	70,638	43,072	1.64

carried out by Uv–Vis and PL spectroscopy. Figure 6a, b presents the absorption and emission spectra of synthesized PIs P1-P4. The absorption spectra of thin films and solution in NMP were recorded at room temperature as shown in Fig. 6a. The absorption spectra of all PIs are almost identical and one absorption maximum with a slight shoulder was observed from 271 to 284 and 339 to 353 nm respectively. The absorption maxima towards the higher energy originated from the π to π^* transitions whereas the shoulder peak towards lower energy region originated from n- π^* transitions of lone pair of electrons of TPA group. Similarly, solid state thin films of PIs (P1-P4) exhibited double absorbance with absorption maxima from 261 to 289 nm and a shoulder band was observed around 338–379 nm.

The photoluminescence study of these PIs was carried out with excitation wavelength corresponding to the maximum absorption wavelength of the PIs. The emission was in violet-blue region with emission maxima at 440,424,414, and 420 nm for P1, P2, P3, and P4 respectively as illustrated in Fig. 7a, b. The emission bands are sharp and narrow and also displayed the blue shift as compared to other PIs with naphthoxy pendant group reported earlier [20]. Besides this blue emission is in well accordance to the TPA based polymers reported by Kim et al. in which electron withdrawing (CF_3) is used as pendant group [16]. P1 displayed red shift as compared to other members of the series whereas P3 showed blue shift which is attributable to the better conjugation in main chain of P1 and the bulky conjugation disruptive hexafluoroisopropylidene group respectively. The PL emission spectra of thin films displayed an additional shoulder emission bands with bathochromic shift which

Table 2 Table solubility data of polyimides P1-P4

Code	NMP	DMAc	DMSO	*m*-Cresol	$CHCl_3$	THF
P1	++	+	±	+	_	_
P2	++	+	±	++	_	_
P3	++	++	+	++	+	_
P4	++	++	±	++	_	_

++ Soluble at room temperature
+ Partially soluble on heating
± Partially soluble at room temperature
_ Insoluble at heating

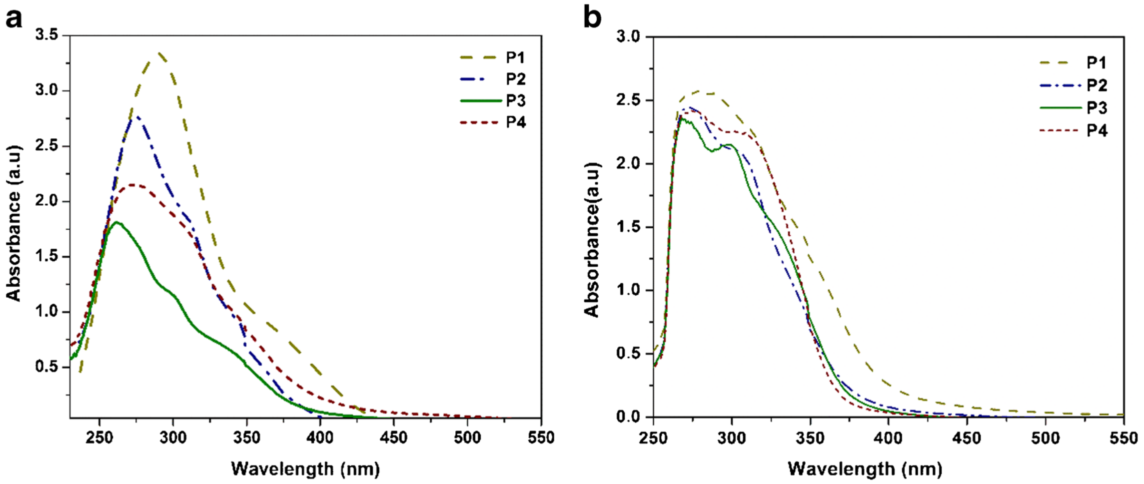


Fig. 6 **a** UV–vis absorption spectra thin films **b** UV–vis absorption spectra of PIs in NMP solution P1-P4

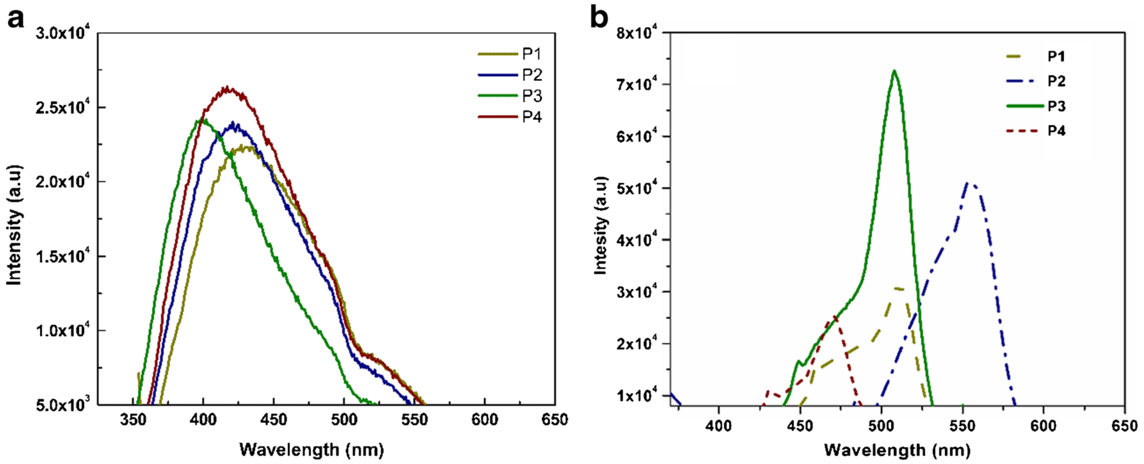


Fig. 7 **a** PL emission spectra thin films **b** PL emission spectra of PIs solution P1-P4

is due to excimer emission as also discussed in our previous article with carbazole–TPA based blue light emitting polyimides [26, 27] (Fig. 7a). The different polarities of the environment, increased conjugation and restricted molecular transitions causing better arrangement of molecules are the factors which may cause bathochromic shift in thin films. As revealed in Fig. 7, the reasonable emission intensity in PI films is displayed.

The PL quantum yields of all prepared PIs (P1-P4) were also calculated by using following equation.

$$\varphi_{\mathrm{unk}} = \varphi_{\mathrm{std}}\left(\frac{\mathrm{I}_{\mathrm{unk}}}{\mathrm{A}_{\mathrm{unk}}}\right)\left(\frac{\mathrm{A}_{\mathrm{std}}}{\mathrm{I}_{\mathrm{unk}}}\right)\left(\frac{\eta_{\mathrm{unk}}}{\eta_{\mathrm{std}}}\right)$$

PL efficiency of quinine sulfate in 1 *N* H_2SO_4 solution was assumed to be 0.54, at 350 nm excitation, where φ_{unk} is the fluorescence quantum yield, (unk and, std in subscript indicates standard i.e. quinine sulfate and unknown sample i.e. PIs), *I* represents the integrated emission intensity and η indicates the refractive indices of the corresponding solutions which was taken to be the same as that of pure solvent. PL quantum efficiencies were found to be 1.6, 1.8, 3.0, and 3.5 for PIs, P1, P2, P3, and P4 respectively. Relatively higher PL quantum yields were observed for P3 and P4 as compared to the rest of the polyimides. The lower PL efficiencies in NMP solution may be ascribed to the fast interconversion from the emissive excited state to the lower emissive state, caused by highly polar NMP solvent. This could also be attributed to the formation of an intermolecular charge transfer (CT) complex that may causes the non-radiative energy transfer, a common observation in aromatic PIs [28, 29]. Moreover, the reduced PL quantum yields may also be ascribed to electron withdrawing 4-quinoline-8-yloxy groups acting nature.

These results depict the blue light emitting properties of the PIs in NMP solution whereas significant blue-green

Table 3 Photophysical properties of P1-P4

Codes	λ_{max} (nm) film	λ_{max} (nm) soln.	λ_{onset} (nm)	$\lambda_{emis.}$ (soln) (nm)	$\lambda_{emis.}$ (film) (nm)	Stoke shift(nm)	Φ %
P1	289, 379	284, 353	431	440	469, 512	87	1.6
P2	275, 348	274, 350	408	424	556	74	1.8
P3	272, 359	271, 344	429	414	435, 471	70	3.0
P4	261, 338	274, 339	456	420	507	81	3.5

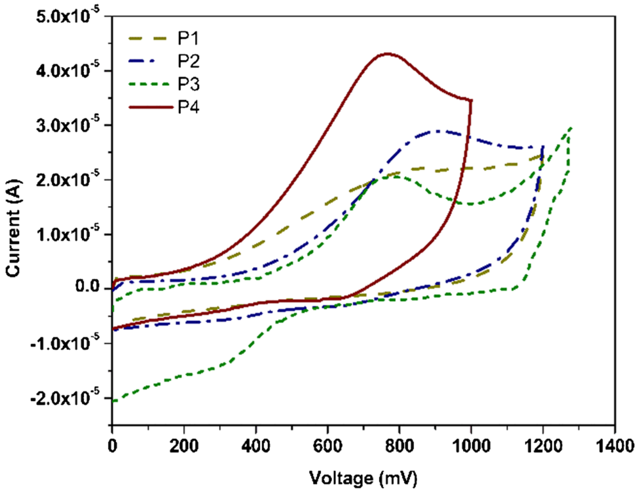


Fig. 8 Cyclic voltammograms of PIs P1-P4

emission in thin films makes these materials appropriate for optical devices (Table 3).

Electrochemical Properties of PIs (P1-P4)

In order to investigate the electrochemical properties of PIs P1-P4, cyclic voltammetry of PIs film using ITO coated glass as substrate was employed while using 0.1M lithium perchlorate as supporting electrolyte, ferrocene/ferrocenium (Fc) redox system as an internal standard at a potential scan rate (50 mV/s) under nitrogen atmosphere. The cyclic voltammograms displayed in Fig. 8 are evident of a single redox couple for all PIs. During anode scan, the onset oxidation potentials for P1-P4 were found as 0.33, 0.37, 0.41, and 0.35 V for P1, P2, P3 and P4 respectively as enlisted in Table 4. These PIs exhibited lower oxidation potentials as compared to traditional PIs as well as our previously reported TPA based PIs having naphthoxy pendant group [20, 30].

The desired lower oxidation potential of these PIs can be attributed to out of plane lone pair of electrons residing on nitrogen atom of pyridine ring thus making it more basic in nature as compared to TPA linkage. These results are in good agreement with other materials published elsewhere [31].

Table 4 Electrochemical data of PIs P1-P4

Code	E_g	E_{onset} V	HOMO eV	LUMO eV
P1	2.87	0.34	−4.74	−1.9
P2	2.92	0.37	−4.77	−1.85
P3	2.99	0.41	−4.81	−1.82
P4	2.71	0.35	−4.75	−2.04

The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV). ELUMO = EHOMO − Eg; Eox/onset (Fc/Fc vs. Ag−AgCl)

Furthermore, E_{onset} values were employed to determine the values of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (versus vacuum) on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level with $E_{onset} = 0.45$ V, as shown in the equations below:

$$E_{\mathrm{HOMO}} = -e\left[E_{\mathrm{onset}} + 4.4\right]\mathrm{eV}$$
$$E_{\mathrm{LUMO}} = E_g - E_{\mathrm{HOMO}}$$

The values of the HOMO level are found in the range (−4.74 to −4.78 eV) for all the newly synthesized PIs as provided in Table 4. These values of HOMO levels are in well accordance with the hole transporting /injection materials in OLEDs materials reported elsewhere [32]. Our presented polyimides possess lower oxidation potentials with shallower HOMO energy levels when compared to other TPA based polyimides (−5.45 to −5.49 eV). Thus, these PIs can be strong candidate for the facile hole injection in electronic devices [33–36].

Conclusions

A series of novel electroactive, fluorescent PIs bearing 4-quinoline-8-yloxy as a pendant group in triphenylamine have been synthesized from the N^1-(4-aminophenyl)-N^1-(4-(quinolin-8-yloxy)phenyl) benzene-1,4-diamine (**4**).The combination of

4-quinolin-8-yloxy (pyridine and ether moieties) with bulky TPA group incorporated a nice balance of different properties in polyimides. The presence of pyridine like ring in the polyimides facilely tunes the onset oxidation potentials hence imparting hole transporting properties in these systems. Additionally, this not only facilely tunes the HOMO levels but also imparts violet emission properties. Besides, these polyimides also displayed a needed combination of properties desirable for the optoelectronic materials which includes good organo-solubility, hence, film forming ability. Thus, these characteristics suggest the potential use of these materials as future fluorescent and optoelectrical applications.

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