

Synthesis, photophysical and electrochemical properties of polyimides of tetraaryl imidazole

A. Hariharan^{1,3} · S. Kumar² · M. Alagar³ ·
K. Dinakaran² · K. Subramanian¹

Received: 6 January 2017 / Revised: 30 March 2017 / Accepted: 3 April 2017 /
Published online: 13 April 2017
© Springer-Verlag Berlin Heidelberg 2017

Abstract The new tetraaryl substituted imidazole-based diamines were designed and synthesized through Debus–Radziszewski imidazole synthesis, and characterized by FT-IR, ¹H NMR spectroscopy and MASS spectroscopy. A series of new fluorescent polyimides (PI) were prepared by polymerization of the tetra substituted imidazole diamines with tetracarboxylic dianhydrides, such as pyromellitic dianhydride, naphthalene tetra carboxylic dianhydride and perylene tetra carboxylic dianhydride. These polymers were readily soluble in a variety of organic solvents and they also possess good thermal stability. The glass transition temperature of these polymers was in the range of 398–453 °C. The ultraviolet–visible absorption spectra showed that all of the polymers had absorption maxima around 344–521 nm with a fluorescence emission maxima around 420–531 nm. The electrochemical band gaps of PI-1, PI-2 and PI-3 copolymers are estimated to be 2.37, 2.17 and 2 eV, respectively. Similarly, the optical band gap of PI-1, PI-2 and PI-3 copolymers was found to be 3.15, 3.05, and 2.15 eV, respectively. These polymer exhibits fluorescence quantum yield of 0.65, 0.46, and 0.3% for PI-1, PI-2 and PI-3, respectively. The PIs also exhibited good flame retardant behavior.

Keywords Polyimides · Imidazole · Debus–Radziszewski imidazole synthesis · Band gap · Fluorescent polymer

✉ K. Dinakaran
kdinakaran.tvu@gmail.com

✉ K. Subramanian
kathsubramanianannauniv@gmail.com

¹ Department of Chemistry, Anna University, Chennai 600025, India

² Department of Chemistry, Thiruvalluvar University, Vellore 632115, India

³ CoExAMMPC, Vignan's FSTR University, Vadlamudi, Guntur 522213, India

Introduction

Aromatic polyimides are commercially important materials that are used extensively in a wide range of optoelectronic applications due to their excellent chemical, thermal, and dielectric properties [1–3]. Despite their outstanding properties, most of the conventional aromatic polyimides have high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents because of their rigid backbones and strong interchain interactions. Thus, polyimide processing is generally carried out via poly(amic acid) precursor, and then converted to polyimide by vigorous thermal or chemical cyclodehydration [1, 4]. However, this process has inherent problems such as emission of volatile by-products and storage instability of poly(amic acid) solution. Recently, significant research has been focused on to design the structural features of polyimide to meet the easy processing and enhance thermal, and optoelectronic properties. Some of the approaches employed to modify the structure are introducing thermally stable moiety, such as rigid aryl groups in the side chain which decrease close-packing in the polymer backbone and lead to enhanced solubility of the polymer, flexible segments, large polar triaryl imidazole pendants and, disruption of symmetry and recurrence of regularity through copolymerization [5–11], and introduction of noncoplanar [12–14] and alicyclic units [15].

Among these approaches, introducing bulky pendent substituent and heteroaromatic rings into polyimide chains, namely imidazole compounds have attracted significant interest because of their widespread biological activities, such as herbicidal [16], fungicidal [17], and anti-inflammatory activities [18] and their use in synthetic chemistry [19]. In addition, they are applied in photography as photosensitive compounds [20]. Therefore, the synthesis of polyimides having heterocyclic rings has been attracted considerable interest.

Akutsu et al. [21] synthesized triaryl imidazole bearing polyimides having glass transition temperatures (T_g) in the range of 279–353 °C, and weight residues at 600 °C were above 82%. The polymers also have good solubility in pyridine and *m*-cresol. Ghaemy et al. [22] synthesized polyimides from unsymmetrical diamine monomer containing triaryl imidazole as pendant group. PIs exhibited excellent solubility in aprotic polar solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), pyridine and methyl sulfoxide (DMSO). Those PIs showed high glass transition temperatures between 230 and 320 °C. Recently, Rafiee et al. [23] reported that the introduction of triaryl imidazole molecules as pendant in polyimide resulted in good solubility, with a glass transition temperature of 264 °C and having UV–Vis absorption maxima around 320 nm and fluorescence emission maxima around 388–407 nm. In the present work, we have synthesized new polyimides by introducing tetraaryl imidazoles in the polyimide backbone, as a maiden attempt, anticipating that the introduction of tetraaryl imidazole, particularly in the main chain will impart solubility, thermal as well as excellent electrochemical properties. The synthesized polyimides exhibited increased value of glass transition temperature, in the range of 398–453 °C. The ultraviolet–visible absorption spectra showed that all of the

polymers had absorption maxima around 344–521 nm with a fluorescence emission maxima around 420–531 nm. The electrochemical band gaps of PI-1, PI-2 and PI-3 copolymers are estimated to be 2.37, 2.17 and 2 eV, respectively. This was designed for the low cost and for large-area employments in optoelectronic devices, such as ambipolar field effect transistors, solar cells, light-emitting devices and electrochromic devices.

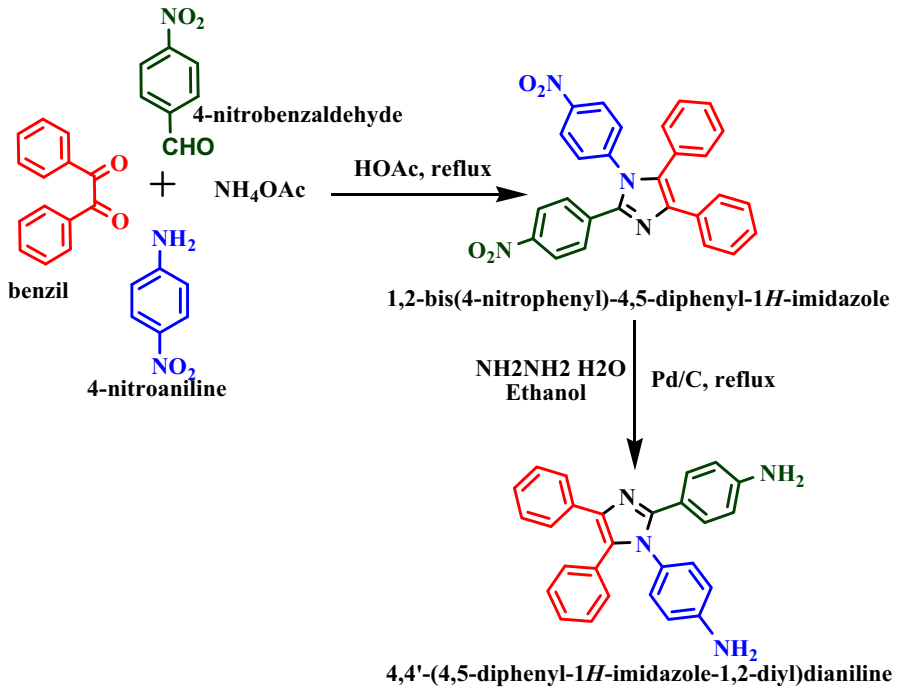
Experimental

Materials

4-Nitrobenzaldehyde (99%) and 4-nitroaniline (purchased from Spectrochem, Benzil, hydrazine HCl, palladium–carbon, *N*-methylpyrrolidone (NMP) (99%) from SRL, acetic acid, ammonium acetate, tetrahydrofuron (THF) (99%), ethanol and methanol (99.8%) were received from Fisher scientific. ^1H NMR (400 MHz) spectra were recorded on a Bruker instrument. Liquid chromatography–mass spectroscopy (LCMS) was measured in an Agilent instrument. FT-IR was recorded in a Perkin Elmer Spectrum RX1 instrument using KBr pellet technique. Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis methods were used to explain the thermal behaviour of the polyimides. TGA was carried out by Hitachi-STA 7200 instrument and DSC carried out by Hitachi-DSC7020 instrument. The optical properties of polyamides were analyzed by UV–Vis and photoluminescence (PL) spectroscopy in THF solution and are presented in Fig. 6. UV–Vis absorption spectra were recorded in a Shimadzu spectrophotometer. PL spectra were carried out by Agilent spectrophotometer. All the polymers were taken about 0.001 mg/mL concentration in THF solvent for UV–Vis and photoluminescence analysis. The cyclic voltammograms of the polymers were done using CH-660D instrument.

Synthesis of 1,2-bis (4-nitrophenyl)-4,5-diphenyl-1*H*-imidazole

In a 100 mL, two-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer and nitrogen gas inlet tube, benzil (1.4 g, 6.6 mmol), 4-nitrobenzaldehyde (1.0 g, 6.6 mmol), 4-nitroaniline (0.9 g, 6.6 mmol) and ammonium acetate (2.3 g, 30 mmol) in 10–15 mL acetic acid were mixed and heated at 120 °C. The progress of reaction was monitored by thin layer chromatography (TLC) in 75:25 hexane ethyl acetate eluting solvent. After completion of reaction, the reaction mixture was cooled to room temperature. Then the product was filtered, washed with water and recrystallized from ethanol to afford 2.2 g (73%) of 1,2-bis (4-nitrophenyl)-4,5-diphenyl-1*H*-imidazole as yellow solid. FT-IR (KBr, cm^{-1}): 3052 (aromatic C–H); 1599 (C=N); 1517, 1345 (NO_2); ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm) = 6.85 (d, 2*H*), 7.4–7.6 (m, 10*H*), 7.81 (d, 2*H*), 8.02 (d, 2*H*), 8.26 (d, 2*H*) (Scheme 1).



Scheme 1 Synthesis of imidazole monomer

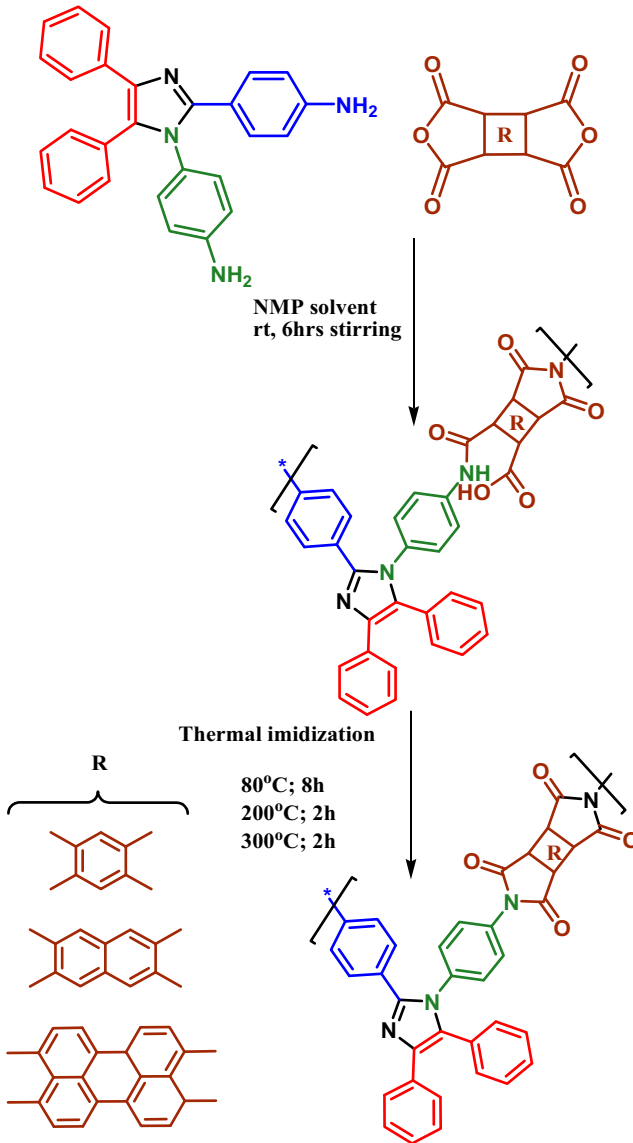
Synthesis of 4,4'-(4,5-diphenyl-1H-imidazol-1,2-diyl)dianiline

To a 50 mL two-necked flask equipped with a dropping funnel and a reflux condenser (1.2 g, 2.5 mmol) of 1,2-bis(4-nitrophenyl)-4,5-diphenyl-1H-imidazole and 50 mg of palladium on activated carbon (Pd/C, 10%) were dispersed in 10 mL of ethanol. The suspension solution was heated to reflux and 4 mL of hydrazine monohydrate was added slowly to the mixture. After refluxing for 5 h THF was added to the mixture and filtered hot to remove Pd/C, and the filtrate was cooled to precipitate orange powder. The product was collected by filtration, recrystallized from ethanol and dried in vacuum at 80 °C [22]. The yield obtained was 67% (0.66 g). FT-IR (KBr, cm^{-1}): 3455, 3352, 3030, 1616, 1506, 1274, 769, 714 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$), The ^1H NMR of imidazole based amine shows signals of protons of N-substituted benzene ring at 5.25 (s, 2H), 5.35 (s, 2H), 6.42 (d, 2H), 6.65 (d, 2H), 6.81 (d, 2H), 7.1–7.6 (m, 10H), 8.25 (d, 2H). ES-MASS (m/z)—401.8.

Synthesis of polyimides

Polyimide was synthesised by two-step thermal imidization reaction. The synthesized diamine (0.1 mol) and dianhydrides (0.1 mol) are dissolved in NMP solvent

and the mixture was stirred at room temperature overnight to obtain polyamic acids. The resulting polyamic acids was then cast on a glass substrate and thermally treated at 80 °C for 8 h, 200 °C for 2 h, and 300 °C for 2 h to obtain the respective cured PIs (Scheme 2).



Scheme 2 Synthesis of imidazole based poly imide

Results and discussion

A new diamine monomer, 4,4'-(4,5-diphenyl-1*H*-imidazol-1,2-diyl)dianiline, was synthesized by a two-step procedure according to the synthetic route shown in Scheme 1. Tetraaryl imidazole based amine was synthesised through Debus–Radziszewski imidazole synthesis [24–26] which involves the condensation of benzil with aromatic aldehyde in the presence of ammonium acetate. The structures of 1,2-bis(4-nitrophenyl)-4,5-diphenyl-1*H*-imidazole and 4,4'-(4,5-diphenyl-1*H*-imidazol-1,2-diyl)dianiline were characterized by FT-IR, ^1H NMR and MASS analyses, the results are presented in Figs. 1, 2 and 3, respectively. Spectral data from the FT-IR and ^1H NMR and MASS analysis show the effective formation of the respective imidazole-based nitro and corresponding amine group. The synthesised amine functionality has been confirmed by IR spectrum. Figure 1 shows the FT-IR spectrum of imidazole based diamine. Diamine functional group has sharp absorption bands at 3455 and 3352 cm^{-1} . The ^1H NMR spectrum shown in Fig. 2. The synthesised imidazole compound has two aniline groups in different environment. One is substituted in Nitrogen atom of imidazole (first position of imidazole) and another one is substituted in carbon atom of imidazole (second position of imidazole). Ha, Hc and He protons belongs to aniline group in first position of imidazole. Similarly Hb, Hd and Hg belongs to aniline group in second position of imidazole. The integral areas of Ha, Hc and He is relatively smaller than that of Hb, Hd and Hg, because of more electronegative and down field desheilding protons resulting from first position of imidazole. The newly synthesised diamine thermally polymerised with three different types of dianhydrides such as pyromellitic dianhydride, naphthalene tetra carboxylic dianhydride and perylene tetra carboxylic dianhydride. The synthesised polyimides were confirmed by IR spectra. Figure 4 shows the FT-IR spectra of PI-1, PI-2 and PI-3. The absorption band at

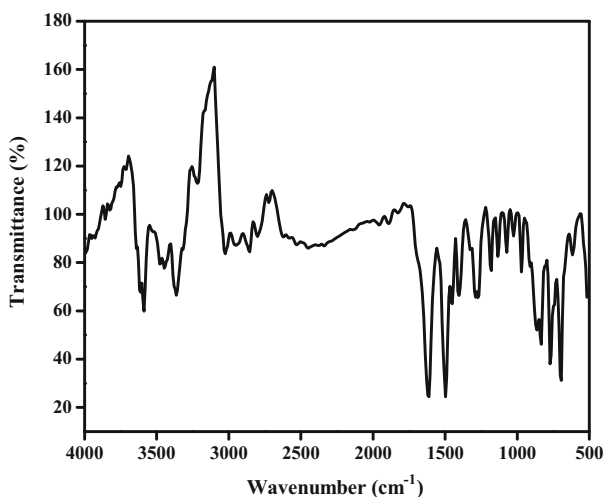


Fig. 1 FT-IR spectrum of tetra substituted imidazole amine monomer

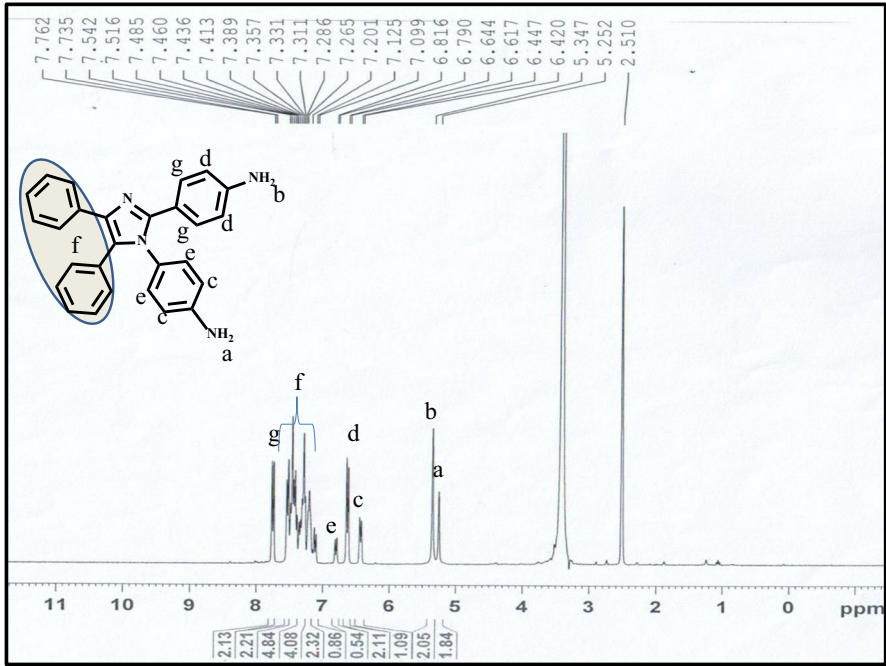


Fig. 2 ¹H NMR spectrum of tetra substituted imidazole amine monomer

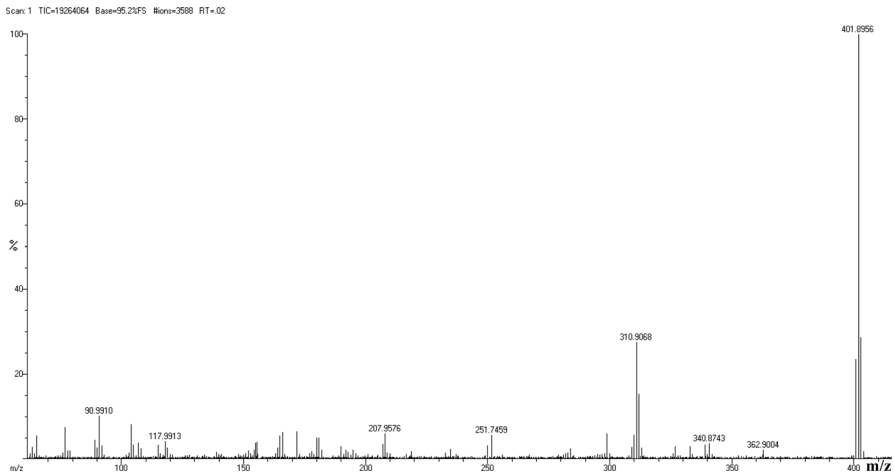


Fig. 3 MASS spectrum of tetra substituted imidazole amine monomer

1768 cm^{-1} confirms the presence of asymmetric stretching vibration of carbonyl —C=O in the imide groups. The absorption band at around 1720 cm^{-1} was due to the symmetrical stretching vibration of imide carbonyl —C=O functionality and the band at 1370 cm^{-1} confirms the presence of imide C—N stretching.

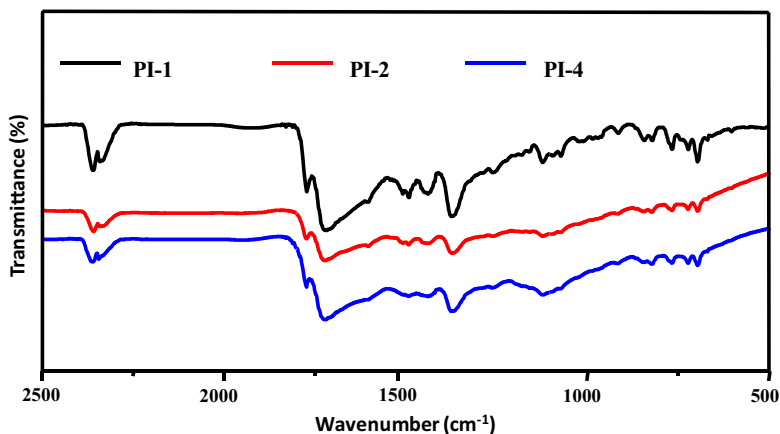


Fig. 4 IR spectra of tetra substituted imidazole based polyimide PI-1, PI-2 and PI-3

Solubility studies

The solubility of imidazole-based polyimides were tested with different common organic solvents such as 1-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF) *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and chloroform (CHCl_3). Table 1 shows the solubility behavior of PIs. The results show that PI-1, PI-2 and PI-3 exhibit good solubility in organic solvents, due to the presence of non-planar imidazole moiety present in the polyimide. It was also found that NMP is the best solvent for polyimides synthesized in the present work.

Thermal behaviour

Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis methods were used to explain the thermal behaviour of the polyimides. TGA was carried out by Hitachi-STA 7200 instrument and DSC carried out by Hitachi-DSC7020 instrument. DSC and TGA thermograms of the polyimides are shown in Fig. 5a, b, respectively. Synthesised polyimide samples were dried for 2 h at 150 °C. Completely dried samples were used for TGA and DSC analysis. The thermal analysis data from the TGA and DSC thermograms of the polyimides are summarized in the Table 2. The T_g values of the polyimides measured by DSC at a

Table 1 Solubility behavior of synthesized PI-1, PI-2 and PI-3 matrix

Samples	Solvents					
	DMAc	DMSO	DMF	NMP	THF	CHCl_3
PI-1	++	++	++	++	++	+-
PI-2	++	++	++	++	++	+-
PI-3	++	++	++	++	++	+-

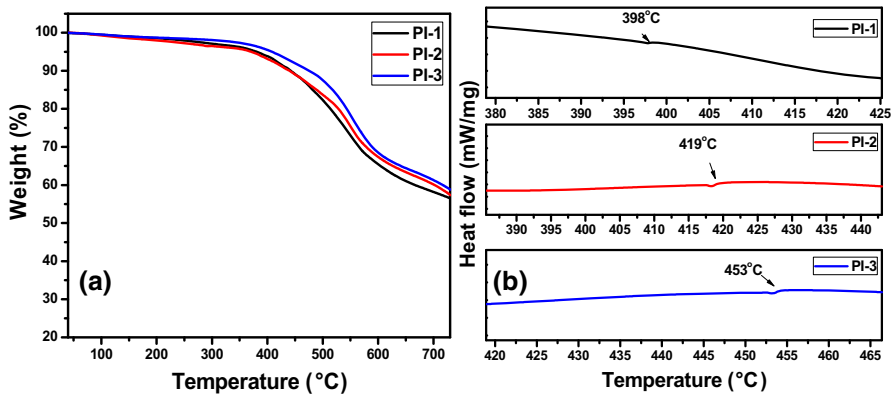


Fig. 5 **a** TGA thermogram of synthesised polyimides PI-1 PI-2 and PI-3. **b** DSC thermogram of synthesised polyimides PI-1 PI-2 and PI-3

Table 2 Thermal property of polyimides PI-1, PI-2 and PI-3

PIs	T_g (°C)	10% weight loss (°C)	T_{max} (°C)	Char yield (%)	LOI
PI-1	398	439	544	56	40
PI-2	419	439	558	58	41
PI-3	453	475	575	60	42

heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The T_g value of the polyimide PI-1, PI-2 and PI-3 were obtained at the range of 398, 419 and $453\text{ }^\circ\text{C}$, respectively. In this DSC thermogram no endothermic peaks associated with melting were observed in the DSC traces. The T_g of polyimide PI-3 ($453\text{ }^\circ\text{C}$) is higher than T_g of the polyimide PI-1 (398) and PI-2 (419) because of the increment of aryl groups. The thermal stability of the polymers was determined by thermogravimetric analysis (TGA) at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere (Fig. 5). Thermal stability of the polymers was calculated in terms of the temperature at 10% weight loss, maximum degradation temperature (T_{max}), char yield at $750\text{ }^\circ\text{C}$ as listed in Table 2. As observed from Fig. 5a, 60% residual weight at $750\text{ }^\circ\text{C}$ of PI derived from perylenetetracarboxylic dianhydride had the highest values in comparison with other PI-1 and PI-2 at 56, 58%, because of the very rigid dianhydride monomer and aggregation of the polymer chain. The high char yields of these polymers could be attributed to their high aromatic content. The T_{max} of the polymers was measured at 544, 558 and $575\text{ }^\circ\text{C}$. Limiting oxygen index (LOI) was estimated according to the Van Krevelen and Hoftzyer equation [27–29]:

$$\text{LOI} = 17.5 + 0.4\text{CR},$$

where CR is the percentage of polymer remaining at $750\text{ }^\circ\text{C}$. All polymers have LOI more than 35 and such polymers can act as flame-retardant materials. The LOI of PI, PI-2 and PI-3 estimated at 40 and 41 and 42, respectively.

Optical behaviour

The optical properties of polyamides were analyzed by UV–Vis and photoluminescence (PL) spectroscopy in THF solution and are presented in Fig. 6. All the polymer samples are prepared by taking about 0.001 mg/mL in THF solvent for UV–Vis and photoluminescence analysis. The absorption maxima for PI-1, PI-2 and PI-3 are 344, 364, and 521 nm, respectively. The broader absorption peak of PI-3 at 521 nm obtained due to presence of perylenetetracarboxylic dianhydride structure in the backbone of these polymers. The longer absorption bands for the polyimide copolymer systems may be explained due to the intramolecular charge transfer between donors and acceptor moieties in the polymer network. The PI-1 polyimide copolymer of pyromellitic dianhydride and tetrasubstituted imidazole absorbs at 344 nm and emits at 429, 405, 452, 539 nm. Similarly, PI-2 polyimide based on naphthalene and tetrasubstituted imidazole amine synthesised showed multiple absorption bands at 355, 364 nm and emission bands at 436, 415, 460, 500, 537 nm. PI-3 polyimide also showed multiple absorption bands at 457, 485, 521 and emission bands at 531, 566, 610 nm. These multi band absorption and emission peaks may be due to the presence of many aryl substituent. In general naphthalene- and perylene-based systems will show strong multi absorption band due to conjugation of poly aryl molecule π - π^* transition, which corresponding polyimide also had strong multi absorption and red shifted due to aryl substituted imiazole influence. These polymers have small absorption n - π^* transition for carbonyl (C=O) and imine (N=C) group. Iqbal et al. [30] reported the optical behavior of polyimides with noncoplanar carbazole–triphenylamine unit and pyromellitic dianhydride has an absorption of 264 and 353 nm and emission at 447 and 490 nm. Similar results of multi band absorption and emission has been reported for polyimide having naphthalene and perylene units.[31, 32] photoluminescence quantum yield and band gap of PI-1, PI-2 and PI-3 were calculated by UV–Vis and

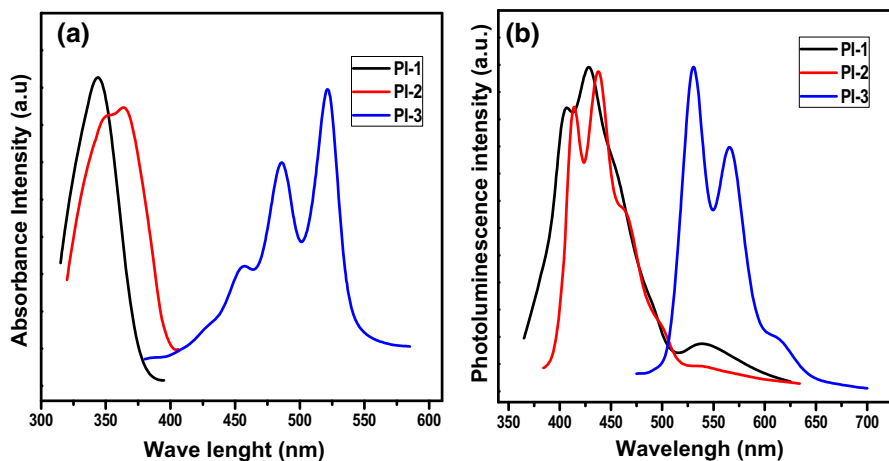


Fig. 6 **a** UV–Vis spectrum of polyimides in THF; **b** photoluminescence of polyimide in THF

photoluminescence spectroscopy. [33–39] The calculated band gaps (E_g) for PI-1, PI-2, and PI-3 were 3.15, 3.05, and 2.15 eV, respectively, since polymer with extended conjugation and stronger acceptor moiety PI-3 found to have low band gap. Single phenylene ring-based pyromellitic dianhydride act as strong acceptor. Similarly two phenyl ring fused naphthalene tetra carboxylic dianhydride is strong electron acceptor moiety then single ring dianhydride and also perylene tetra carboxylic dianhydride act as very strong acceptor than other two anhydrides because it has more bulky dianhydride moiety. During the improvement of the electron delocalisation or electron donor acceptor segments band gap energy of the polymeric material may get lower. Here electron acceptor property improved from PI-1 to PI-3. From these results perylene-based PI-3 have lower band gap than other PIs.

To measure the photoluminescence quantum yields (Φ^{PL}), [36–39] dilute polymer solutions in THF were used. Rhodamine 6G ($\Phi^{PL} = 0.95$) was used as a reference [33, 36–39]. The emission spectrum of polymer PI-1, PI-2 and PI-3 were recorded under excitation wavelength in the maximum of the absorption band, i.e., 430, 440 and 531 (563) nm, respectively. The emission wavelengths were observed at 344–521 nm. The quantum yield of polyimides summarized in Table 3 and the PL spectrum of all polymers are presented in Fig. 6b.

Electrochemical properties

It is known that energy-level is important parameter for optoelectronic device; the energy-level band gap of the polymers was calculated using cyclic voltammeter (CV). The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. All measurements were performed using acetonitrile solution of 0.1 M Bu₄N(ClO₄) as a supporting electrolyte with a scan rate of 50 mV s⁻¹. All the potentials were calibrated with ferrocene as an

Table 3 Optical and electrochemical property of polyimides

Sample name	Optical property				Electrochemical property		
	Absorption ($\lambda_{max}/\lambda_{onset}$) (nm)	Emission (λ_{max}) (nm)	$E_g^{opt.}$ (eV) ^a	Φ^{PLb}	Redox _{onset}	HOMO (eV)	LUMO (eV)
PI-1	344/392	429 (405, 452, 539)	3.15	0.65	-1.10	-6.45	-3.30
PI-2	364/406	436 (415, 460, 500, 537)	3.05	0.46	-0.99	-6.46	-3.41
PI-3	(521) 457, 485/565	531 (566, 610)	2.15	0.30	-0.95	-5.60	-3.45

^a Calculated from the onset wavelength of corresponding UV–Vis absorption spectrum, $E_g^{opt.} = 1240/\lambda$ (nm) eV

^b Quantum yield estimated from photoluminescence emission spectrum in THF and Rhodamine 6G in ethanol was taken as the standard ($\Phi_{PL} = 0.94$)

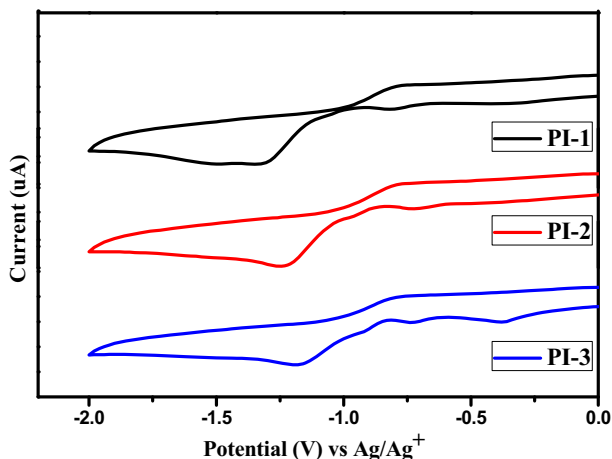


Fig. 7 Cyclic voltammograms of polyimides PI-1, PI-2 and PI-3. Samples was carried out using ACN, 0.1 M $\text{Bu}_4\text{N}(\text{ClO}_4)$ electrolyte and scan rate at 50 mV s^{-1}

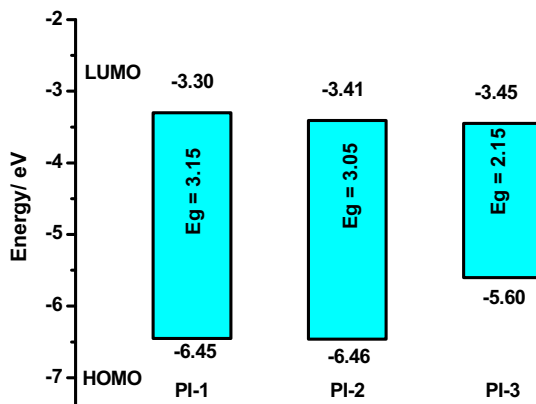
external standard. The voltammograms are shown in Fig. 7. The LUMO energy levels are estimated by the onset of reduction potential and the onset reduction potential were recorded to be -1.1 , -0.99 , and -0.95 V ; thus, the corresponding LUMO energy levels of PI-1, PI-2, and PI-3 are -3.30 , -3.41 , and -3.45 eV , respectively. LUMO levels were calculated from onset of reduction with the following equation [33, 38–41]

$$E_{\text{LUMO}} = -E_{\text{red/onset}} - 4.4 \text{ eV}.$$

The HOMO levels were calculated from LUMO and optical band gap. HOMO energy levels of PI-1, PI-2, and PI-3 were calculated at -6.45 , -6.46 , and -5.60 eV , respectively. Similar results were recorded and published by Chen et al., and Hsiao et al., Hu et al. [[9, 42, 43] it is evidenced that the introduction of tetra substituted imidazole group on polyimide has good impact on its HOMO–LUMO energy level as shown in Fig. 8. Structures of the dianhydrides reveal that pi electron delocalization is in the order of $\text{PI-1} < \text{PI-2} < \text{PI-3}$ which influence the energy separation values between the HOMO and LUMO. The aromatic rings increasing from PI-1 to PI-3. Hence Energy gap of HOMO/LUMO has decreases from PI-1 to PI-3. These results reveals that the synthesized polyimides are may be suitable to be used in ambipolar field effect transistors, solar cells, light-emitting devices and electrochromic devices.

From a materials point of view, the active semiconductors are required to have HOMO energy levels below -6.0 eV for stable hole transport, and the LUMO level needs to be close to or below -3.0 eV for stable electron transport. Therefore, the energy gap between the HOMO and LUMO levels should not be too large to avoid charge injection barriers. The development of novel strong electron-withdrawing building blocks plays an essential role for such applications.

Fig. 8 The HOMO–LUMO energy level of PI-1, PI-2 and PI-3



Conclusion

The new tetrasubstituted imidazole diamine monomer was successfully synthesized with high purity and characterized. Aromatic polyimides PI-1, PI-2 and PI-3 were successfully synthesised through polycondensation reaction of tetra substituted imidazole-based diamines with three different dianhydrides. All the polymers were readily soluble in organic polar solvents, such as tetrahydrofuran, CHCl_3 , DMF, DMAc. The DSC and TGA analysis indicated that the synthesised PIs have high thermal stability with higher glass transition temperature than the reported imidazole containing PIs. Among the synthesised polymers, the polymer PI-1 has a low band gap value of 2.37 eV with a photoluminescence quantum yield of 65%.

Acknowledgements The authors acknowledge the financial support of the University Grants Commission, New Delhi, India through grant UGC F. No: 39-784/2010. The author A. Hariharan acknowledges the BSR fellowship from the University Grants Commission, New Delhi, India through grant UGC-BSR doctoral fellowship.

References

- Hu Z, Zhang K, Huang F, Cao Y (2015) Water/alcohol soluble conjugated polymers for the interface engineering of highly efficient polymer light-emitting diodes and polymer solar cells. *Chem Commun* 51:5572–5585
- Gong X, Tong MH, Park SH, Liu M, Jen A, Heeger AJ (2010) Semiconducting polymer photodetectors with electron and hole blocking layers: high detectivity in the near-infrared. *Sensors* 10:6488–6496
- Li L, Zhang F, Wang W, An Q, Wang J, Sun Q, Zhang M (2015) Improved performance of photomultiplication polymer photodetectors by adjustment of P3HT molecular arrangement. *ACS Appl Mater Interfaces* 7:5890–5897
- Li C, Mao Z, Chen H, Zheng L, Huang J, Zhao B, Tan S, Yu G (2015) Synthesis, characterization, and field-effect transistors properties of novel copolymers incorporating nonplanar biindeno[2,1-*b*]thiophenylidene building blocks. *Macromolecules* 48:2444–2453
- Zhao J, Peng L, Zhu YL, Song YJ, Wang LJ, Shen YZ (2016) Synthesis and memory characteristics of novel soluble polyimides based on asymmetrical diamines containing carbazole. *Polymer* 91:118–127

6. Rafiee Z, Golriz L (2014) Synthesis and properties of thermally stable polyimides bearing pendent fluorene moieties. *Polym Adv Technol* 25:1523–1529
7. Chern YT, Tsai JY (2008) Low dielectric constant and high organosolubility of novel polyimide derived from unsymmetric 1,4-bis(4-aminophenoxy)-2,6-di-tert-butylbenzene. *Macromolecules* 41:9556–9564
8. Rafiee Z, Khalili S (2013) Synthesis and characterization of highly soluble and thermally stable new polyimides based on 3,5-diamino benzoyl amino phenyl-14*H*-dibenzoxanthene. *Polym Bull* 70:2423–2435
9. Hsiao SH, Wang HM, Chen WJ, Lee TM, Leu CM (2011) Synthesis and properties of novel triptycene-based polyimides. *J Polym Sci A Polym Chem* 49:3109–3120
10. Chen JC, Wu JA, Li SW, Chou SC (2014) Highly phenylated polyimides containing 4,4'-diphenylether moiety. *React Funct Polym* 78:23–31
11. Yang Z, Chen Y, Wang Q, Wang T (2016) High performance multiple-shape memory behaviors of poly(benzoxazole-*co*-imide)s. *Polymer* 88:19–28
12. Liu C, Wang J, Lin E, Zong L, Jian X (2012) Synthesis and properties of phthalonitrile-terminated oligomeric poly(ether imide)s containing phthalazinone moiety. *Polym Degrad Stab* 97:460–468
13. Liu C, Pei X, Huang X, Wei C, Sun X (2015) Novel non-coplanar and tertbutyl-substituted polyimides: solubility, optical, thermal and dielectric properties. *Chin J Chem* 33:277–284
14. Liaw DJ, Chang FC, Leung MK, Muellen K (2005) High thermal stability and rigid rod of novel organosoluble polyimides and polyamides based on bulky and noncoplanar naphthalene-biphenyl-diamine. *Macromolecules* 38:4024–4029
15. Yamada M, Kusama M, Matsumoto T, Kurosaki T (1993) Soluble polyimides with polyalicyclic structure. 2. Polyimides from bicyclo[2.2.1]heptane-2-*exo*-3-*exo*-5-*exo*-6-*exo*-tetracarboxylic 2,3:5,6-dianhydride. *Macromolecules* 26:4961–4963
16. Liebl R, Randte R, Mildenerger H, Bauer K, Bieringer H (1987) Preparation and characterization of polyimides containing triaryl imidazole side groups. *Ger Offen DE*, 3604 042, Aug. 13 (Chem. Abstr. 108, 1988, 6018 g)
17. Pozhetskii AF, Soldatenkov AT, Katritzky AY (1997) *Heterocycles in life and society*. Wiley, New York
18. Lambardino JG, Wiseman EH (1974) Preparation and antiinflammatory activity of some nonacidic trisubstituted imidazoles. *J Med Chem* 17:1182–1188
19. Heravi MM, Bakhtiari K, Oskooie HA, Taheri S (2007) Synthesis of 2,4,5-triaryl-imidazoles catalyzed by NiCl₂·6H₂O under heterogeneous system. *J Mol Catal A Chem* 263:279–281
20. Yang WH, Xiao GM (2002) Efficient improved synthesis of 2-aryl-4,5-diphenylimidazole by heating. *Chin Fine Chem* 19:155–157
21. Akutsu F, Inoki M, Sawano M, Kasashima Y, Naruchi K, Miura M (1998) Preparation and characterization of novel aromatic polyimides having 4,5-di(1,3-phenylene)imidazole structure. *Polymer* 39:6093–6098
22. Ghaemy M, Alizadeh R (2009) Synthesis of soluble and thermally stable polyimides from unsymmetrical diamine containing 2,4,5-triaryl imidazole pendent group. *Eur Polym J* 45:1681–1688
23. Rafiee Z, Rasekh M (2016) Preparation and characterization of polyimides containing triaryl imidazole side groups. *Polym Adv Technol* 27:533–540
24. Zolfigol MA, Baghery S, Moosavi-Zare AR, Vahdat SM (2015) Synthesis of 1,2,4,5-tetrasubstituted imidazoles using 2,6-dimethylpyridinium trinitromethanide [2,6-DMPyH]C(NO₂)₃ as a novel nanostructured molten salt and green catalyst. *RSC Adv* 5:32933–32940
25. Das PJ, Das J, Ghosh M, Sultana S (2013) Solvent free one-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by secondary amine based ionic liquid and defective Keggin Heteropoly acid. *Green Sustain Chem* 3:6–13
26. Kumar D, Thomas KRJ (2011) Optical properties of pyrene and anthracene containing imidazoles: experimental and theoretical investigations. *J Photochem Photobiol A Chem* 218:162–173
27. Kulhanek J, Bures F (2012) Imidazole as a parent π -conjugated backbone in charge-transfer chromophores. *Beilstein J Org Chem* 8:25–49
28. Jaber ZK, Barekat M (2010) One-pot synthesis of tri- and tetra-substituted imidazoles using sodium dihydrogen phosphate under solvent-free conditions. *Chin Chem Lett* 21:1183–1186
29. Boopathy M, Subramanian K (2016) Studies on photocrosslinking and flame-retardant properties of chalcone-based polyacrylamides. *Polym Adv Technol* 27:466–476

30. Iqbal A, Lee SH, Park OO, Siddiqi HM, Akhter T (2016) Synthesis and characterization of blue light emitting redox-active polyimides bearing noncoplanar fused carbazole-triphenylamine. *New J Chem* 40:5285–5293
31. Damaceanu MD, Rusu RD, Bruma M, Jarzabek B (2010) Blue fluorescent polyamides containing naphthalene and oxadiazole rings. *J Polym* 42:663–669
32. Do JY, Jang B (2013) The efficient synthesis of N-fused coronene analogs and a related polyimide with near-infrared absorption. *Polym J* 45:1177–1182
33. Lindner JP (2016) Imidazolium-based polymers via the poly-Radziszewski reaction. *Macromolecules* 49:2046–2053
34. Faghihi K, Ashouri M, Feyzi A (2013) Synthesis and characterization of new polyimide/organoclay nanocomposites containing benzophenone moieties in the main chain. *J Mex Chem Soc* 57:133–136
35. Revathi R, Prabunathan P, Devaraju S, Alagar M (2015) Synthesis of soluble polyimides based on ether-linked cyclohexyldiamine and their ultraviolet shielding behavior. *High Perform Polym* 27:247–253
36. Kato SI, Yamada Y, Hiyoshi H, Umezu K, Nakamura Y (2015) Series of Carbazole–pyrimidine conjugates: syntheses and electronic photophysical, and electrochemical properties. *J Org Chem* 80:9076–9090
37. Sharma BK, Shaikh AM, Agarwal N, Kamble RM (2016) Synthesis, photophysical and electrochemical studies of acridone-amine based donor–acceptors for hole transport materials. *RSC Adv* 6:17129–17137
38. Truong MA, Nakano K (2016) Syntheses of dibenzo[*d,d'*]benzo[2,1-*b:3,4-b'*]difuran derivatives and their application to organic field-effect transistors. *Beilstein J Org Chem* 12:805–812
39. Sharma BK, Shaikh AM, Kamble RM (2015) Synthesis, photophysical, electrochemical and thermal investigation of triarylamine based on 9*H*-Xanthen-9-one: yellow–green fluorescent materials. *J Chem Sci* 27:2063–2071
40. Brouwer AM (2011) Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report). *Pure Appl Chem* 83:2213–2228
41. Wurth C, Gonzalez MG, Niessner R, Panne U, Haisch C, Gengera UR, Resch GU (2012) Determination of the absolute fluorescence quantum yield of rhodamine 6G with optical and photoacoustic methods—providing the basis for fluorescence quantum yield standards. *Talanta* 90:30–37
42. Chen CJ, Hung Ju, Yen HJ, Hu YC, Liou GS (2013) Novel programmable functional polyimides: preparation, mechanism of CT induced memory, and ambipolar electrochromic behavior. *J Mater Chem C* 1:7623–7634
43. Hu YC, Chen CJ, Liou GS (2012) Novel triphenylamine-containing ambipolar polyimides with pendant anthraquinone moiety for polymeric memory device, electrochromic and gas separation applications. *J Mater Chem* 22:20394–20402