Polymer Bulletin (2026) 83:362
https://doi.org/10.1007/s00289-026-06404-7

ORIGINAL PAPER

Sustainable furfural-based (co)poly[(N-arylene diindolylmethane) ketone]s: synthesis, characterization, and post-modification

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Received: 18 October 2025 / Revised: 2 March 2026 / Accepted: 1 April 2026

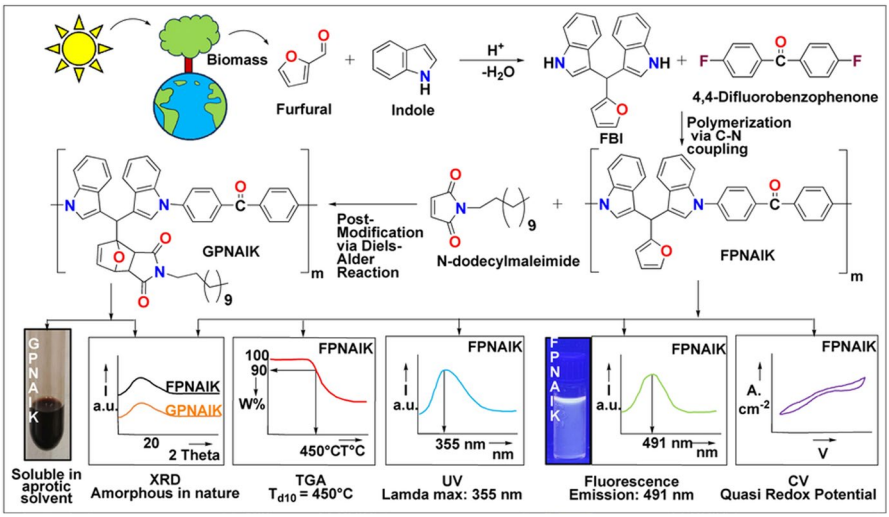
Abstract

A new series of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5) having a pendant clickable furyl group was synthesized through nucleophilic substitution polycondensation by varying molar proportions of renewable furfural-indole based monomer, i.e. 3,3'-(furan-2-ylmethylene)bis(1H-indole) and 3,3-diindolylmethane with 4,4′-difluorobenzophenone. ^{1}H-NMR, ^{13}C-NMR, ^{13}C-DEPT-NMR, Mass and FT-IR spectroscopy confirmed the chemical structures of the synthesized monomers and polymers. The inherent viscosities of all FPNAIKs were determined within the 0.42–0.45 dL/g, indicates formation of moderate molecular weights. The thermal stability of all FPNAIKs showed a T_{d10}% value under N_2 atmosphere in the range 450–470 °C. UV–visible spectrum of FPNAIK showed λ_{max} at 355 nm, and fluorescence spectral studies revealed light green emission. Cyclic voltammetry confirmed the electroactive behaviour of FPNAIK, highlighting their potential applications in optoelectronics devices. Post-modified (co)poly[(N-arylene diindolylmethane) ketone] (GPNAIK) was synthesized from FPNAIK-1 with aliphatic maleimide via Diels–Alder reaction. ^{1}H-NMR and FT-IR spectroscopy confirmed the post-modified GPNAIK chemical structure. This post-modified GPNAIK were soluble in polar aprotic solvents at room temperature. An X-ray diffraction study confirmed that all polymers are amorphous in nature. These research established furyl-indole based polymers as a sustainable approach towards the synthesis of high-performance materials that combine thermal stability, electroactivity, and optical properties for future optoelectronic technologies.

Extended author information available on the last page of the article

Published online: 15 April 2026

Graphical Abstract



Keywords Biobased · Furfural · Indole · Polyindoles · Post-modification

Introduction

Environmental concerns arising from petroleum-based plastics have prompted the conversion of biomass into processable high-performance polymers, fulfilling the global need for sustainable material innovation [1–3]. Conventional high-performance polymers, while valued for their versatility and durability, are hindered by their dependence on fossil resources, poor recyclability, long-term persistence in ecosystems, and limited processability [4–6]. Addressing these issues requires polymers designed within the framework of a circular economy, combining renewable monomers, scalable synthesis, recyclability, and enhanced processability [7–9].

Among biomass-derived building blocks, furfural is an important molecule obtained from hemicellulosic carbohydrates [10–12]. Its furan ring structure provides a renewable analogue to aromatic petrochemicals and offers wide chemical versatility for constructing thermally robust and functional polymers [13–16]. Alongside furans, Indole represents another renewable scaffold, occurring naturally in plants, microbes, and amino acids such as tryptophan, and accessible through biotechnological processes such as fermentation [17, 18]. Its rigid and conjugated framework introduces structural diversity, electronic functionality, and stability into polymer backbones [19–21].

In this work, furfural and indole-derived bis-indole monomers were employed to construct a new series of (co)poly[(N-arylene diindolylmethane) ketone]s bearing pendant furyl groups. These polymers combine the adaptability of furans with the rigidity and conjugation of indoles, producing backbones with promising thermal, optical, and electrochemical characteristics [22–26]. To address the inherent process-

ing limitations of rigid aromatic polymers, post-functionalization was carried out through Diels–Alder reactions with aliphatic maleimides [27, 28]. This modification introduces flexible side chains directly onto the polymer backbone, enhancing solubility, while preserving the high thermal stability [29, 30]. Collectively, this approach demonstrates how renewable feedstocks, when combined with post-polymer modification strategies, can yield processable, high-performance polymers suited for advanced functional and optoelectronic applications.

Experimental

Materials

Furfural was purchased from Sigma Aldrich, distilled under reduced pressure, and kept over 4Å molecular sieves. Indole, salicylic acid (SA), and 4,4-difluorobenzophenone (DFBP) were purchased from Spectrochem and used as received. N-Methyl-2-pyrrolidone (NMP) was purchased from Spectrochem and kept over 4Å molecular sieves. N-Dodecylmaleimide and 3,3-diindolylmethane (DIM) were purchased from BLD Pharma. Solvents such as N, N-dimethylformamide (DMF), Dimethyl Sulfoxide (DMSO), N, N-dimethylacetamide (DMAc), tetrahydrofuran (THF), methanol, ethanol, and chloroform were used without further purification. Potassium carbonate (K_2CO_3) was dehydrated at 150 °C in a vacuum oven for 10 h before use.

Measurements

Fourier transform infrared spectrometry (FT-IR) (Bruker Alpha II) was used to identify the functional groups of precursors and polymers. The Nuclear Magnetic Resonance (NMR) Spectra were recorded on a Bruker Avance Neo spectrometer to analyze the chemical structures. The molecular weight was determined using a Waters Micromass Q-Tof Micro mass spectrometer. Ultraviolet–visible (UV–Vis) spectra were recorded on a SPECORD PLUS UV/Vis double-beam spectrophotometer in diluted NMP solutions (10^{-5} M), using 10 mm quartz cells at room temperature. Fluorescence spectra were obtained using a JASCO Spectrofluorometer FP-8300 under the same conditions. X-ray diffraction (XRD) analysis was carried out on an Ultima IV goniometer. Inherent viscosities were measured with a Ubbelohde suspended-level viscometer. Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 at a heating rate of 10 °C/min under a nitrogen atmosphere. The cyclic voltammograms (CV) were recorded with an AUTOLAB PGSTAT 302N instrument using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode in 1 M H_2SO_4 at a scan rate of 20 mV s^{-1}.

Synthesis of 3,3'-(furan-2-ylmethylene)bis(1H-indole) (FBI)

The bis-indole bearing pendant furan ring was synthesized as per the reported procedure [31]. Indole 23.4 g (0.2 M), furfural 9.6 g (0.1 M), and salicylic acid 2.07 g (15 mol%) were placed in a round-bottom flask, and H_2O: EtOH (1:1, 500 ml) were

added. The reaction mixture was stirred for 2 h at 30 °C. After completion of the reaction, the solid was formed. The resulting solid product was filtered off, washed with distilled water, dried, and recrystallised in ethanol.

Appearance: Red Solid.

Yield: 30.8 g [98.70%].

M.P.: 117 °C.

FT-IR: 3443–3407 cm^{-1} (NH stretching), 3107, 3052, 2923, 2854, 1580, 1453, 1333 $cm.^{-1}$

LC–MS: $C_{21}H_{16}N_2O$, 311.1196 M/z $[M\text{-}H^+]^{+\cdot}$

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 2H, adjacent to N, N–H), 7.46 (d, 2H), 7.33(d, 1H), 7.30 (d, 2H), 7.15 (t, 2H), 7.00 (t, 2H), 6.78(s, 2H), 6.28 (t, 1H), 6.04 (d, 1H), 5.91 (s, 1H methylene bridge C-H).

^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 157.06 (furan C-O), 141.21, 136.49, 126.75, 123.04, 121.94, 119.66, 119.34. 117.13, 111.11, 110.13, 106.60, 34.08 (methylene bridge C-H).

Synthesis of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK)

In a 100 mL three-necked flask under a nitrogen atmosphere, renewable-source-derived 3,3'-(furan-2-ylmethylene)bis(1H-indole) (1.248 g, 4 mmol), 4,4'-difluorobenzophenone (0.872 g, 4 mmol), K_2CO_3 (1.104 g, 8 mmol), and NMP (10 mL) were introduced. The reaction system was continuously evacuated and flushed with high-purity nitrogen. The mixture was then heated at 170 °C and maintained for 10 h under stirring. After completion, the resulting polymer solution was allowed to cool at room temperature and poured into cold water to precipitate the polymer. The precipitated polymer was filtered, thoroughly washed with water and methanol, and dried under vacuum at 100 °C.

The same procedure was employed for the synthesis of a series of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-2 to 5) by varying molar feed ratios of FBI to 3,3'-diindolylmethane (DIM).

FT-IR:**FPNAIK-1:** 3049, 2921, 1656 (Ketone C=O), 1598, 1454 $cm.^{-1}$
FPNAIK-2: 3046, 2920, 1655 (Ketone C=O), 1597, 1454 $cm.^{-1}$
FPNAIK-3: 3049, 2901, 1653 (Ketone C=O), 1597, 1454 $cm.^{-1}$
FPNAIK-4: 3075, 2918, 1652 (Ketone C=O), 1596, 1454 $cm.^{-1}$
FPNAIK-5: 3049, 2929, 1652 (Ketone C=O), 1597, 1454 $cm.^{-1}$

^{1}H-NMR, (400 MHz, $CDCl_3$), FPNAIK-1: δ 7.94 (br m, 4H), 7.6 (br m, 8H Aromatic C-H benzophenone) C-H, 7.43 (br s, 1H), 7.00 (br m, 6H), Furan rings: 6.36 (br s, 1H) and 6.21 (br s, 1H), 6.06 (br s, 1H methylene bridge C-H).

^{13}C-NMR, (100 MHz, $CDCl_3$), FPNAIK-1 δ (ppm): 194.28 (C_a=O ketone), 155.93, 143.41 (C_c-H), 141.81, 136.12, 134.74, 131.82, 128.79, 126.31, 123.31, 123.20, 121.02, 120.38, 119.22, 110.91, 110.49, 107.27, 34.12 (methylene bridge C_r-H).

^{13}C-DEPT-135 NMR, (100 MHz, $CDCl_3$), FPNAIK-1 δ (ppm): 143.41 (C_c-H), 141.81, 136.12, 134.74, 131.82, 128.79, 126.31, 123.31, 123.20, 121.02, 120.38, 119.22, 110.91, 110.49, 107.27, 34.12 (methylene bridge C_r -H).

Synthesis of Post-modified (co)poly[(N-arylene diindolylmethane) ketone]s (GPNAIK)

In a 25 mL three-necked flask equipped with a magnetic stirrer, nitrogen inlet, and water-cooled condenser, FPNAIK-1 (0.490 g, 1.0 mmol), N-dodecylmaleimide (0.265 g, 1.0 mmol), and chloroform (10 mL) were added. The reaction mixture was evacuated and flushed with high-purity nitrogen to ensure an inert atmosphere. The mixture was then stirred at 60 °C for 24 h. After cooling to room temperature, the resulting viscous reaction mixture was poured into excess cold water to precipitate the polymer. The resulting solid was collected by filtration, washed with water and methanol, and dried under vacuum at 70 °C.

Yield: 0.74 g [98.01%].

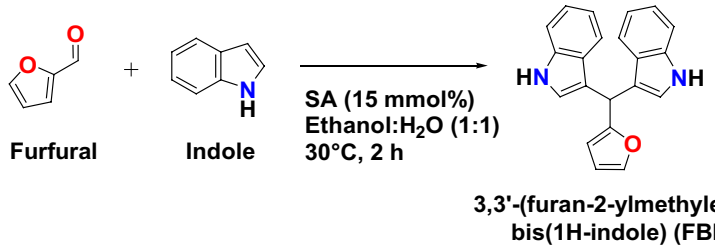
FT-IR: 3046, 2929, 1701 (Imide C=O), 1656 (Ketone C=O), 1594, 1453 $cm.^{-1}$

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (br m, 3H, CH_3), 1.2 (br m, 18H, $(CH_2)_9$), 1.55–1.75 (m, 2H, CH_2), 3.2–3.6 (m, 2H, N-CH_2), 6.8–8.5 (br m, aromatic H), 6.35 (br s, 1H) and 6.20 (br s, 1H), 6.05 (br s, 1H methylene bridge C-H).

Results and discussion

Synthesis of monomer 3,3'-(furan-2-ylmethylene)bis(1H-indole) (FBI)

The bis-indole monomer bearing a pendant furan ring was synthesized via the condensation of indole and furfural in the presence of salicylic acid as a catalyst in a 1:1 water–ethanol medium (Scheme 1). The precipitated product was isolated by filtration and recrystallized from ethanol. The reaction proceeds through an acid-catalyzed electrophilic substitution mechanism. The structure of FBI was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry (Fig. S1-S4).



Scheme 1 Synthesis of 3,3'-(furan-2-ylmethylene)bis(1H-indole) (FBI)

Synthesis of (co)poly[(N-arylene diindolylmethane) ketone]s

In the FPNAIK series (Scheme 2), FPNAIK-1 was synthesized from 3,3′-(furan-2-ylmethylene)bis(1H-indole) (FBI) and 4,4′-difluorobenzophenone (DFBP) through C-N coupling. In a procedure, FBI and DFBP were reacted in NMP with K_2CO_3 at 170 °C for 10 h under nitrogen, yielding FPNAIK-1. The remaining polymers in the FPNAIK series (FPNAIK-2 to FPNAIK-5) were obtained by varying the molar ratios of FBI and 3,3′-diindolylmethane (DIM), as summarized in Table 1. The inherent viscosities of all FPNAIKs were determined within the 0.42–0.45 dL/g. These values indicate the formation of moderate molecular weight polymers under the applied polymerization conditions.

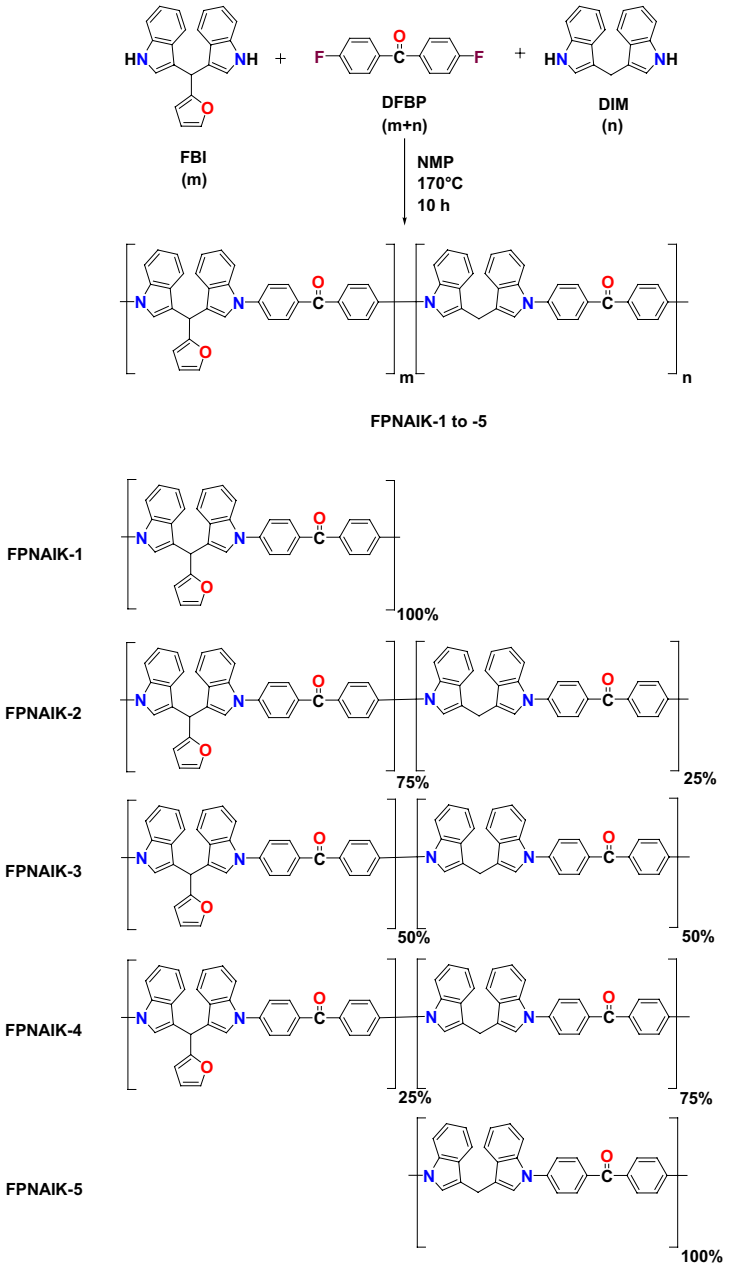
The polymerization proceeds through base-mediated deprotonation of the indolic N–H groups to generate indolide anions (Scheme 3). These anions undergo nucleophilic aromatic substitution at the para-fluoro positions of DFBP. The carbonyl group increases the electrophilicity of the aromatic ring and stabilizes the σ-complex intermediate. Elimination of fluoride forms the C-N bond, resulting in step-growth polymer formation. Reaction at both fluorine sites of DFBP yields linear FPNAIK backbones. The polymerization of FPNAIK-1 method uses biobased furfural-indole precursors and does not require toxic metal catalysts, which may reduce economic and environmental impact. Incorporation of the furyl unit enables post-modification of the polymer through Diels–Alder reaction.

FT-IR of (co)poly[(N-arylene diindolylmethane) ketone]s

The structural features of the synthesized (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5) were confirmed by FTIR spectroscopy (Fig. 1). The spectra exhibited distinct absorptions at 3046 -3075 cm^{-1} and 2901- 2929 cm^{-1}, correspond to the aromatic C-H stretching of indole and phenyl units and the aliphatic C-H stretching of methylene linkages, respectively. A sharp and intense band at 1656–1652 cm^{-1} were assigned to the stretching vibration of the carbonyl (C = O) group derived from the benzophenone moiety, thereby confirm the incorporation of ketone functionalities into the polymers backbone. Additional absorptions observed at 1596–1598 and 1454 cm^{-1} were attributed to C = C stretching vibrations of the aromatic framework, consistent with the presence of a conjugated aryl-indole structures. The absence of the characteristic N–H stretching vibration of free indole units, typically observed in the 3400–3200 cm^{-1} region, provided evidence for the successful participation of the indole nitrogen in the C-N bond-forming reaction with DFBP, thereby validating the proposed polymerization pathway (Fig. S9-S13).

^{1}H-NMR of furyl-(co)poly[(N-arylene diindolylmethane) ketone] FPNAIK-1

The ^{1}H NMR spectrum of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1) bearing a pendant furan ring (FPNAIK-1) exhibited the proposed structural framework containing bis-indole units, benzophenone spacers, and a pendant furan moiety (Fig. 2). The most deshielded signal at δ 7.94 (4H) is assigned to the aromatic protons '$\mathbf{H_a}$' adjacent to the indolic nitrogen, reflect the strong anisotropic



Scheme 2 Synthesis of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5)

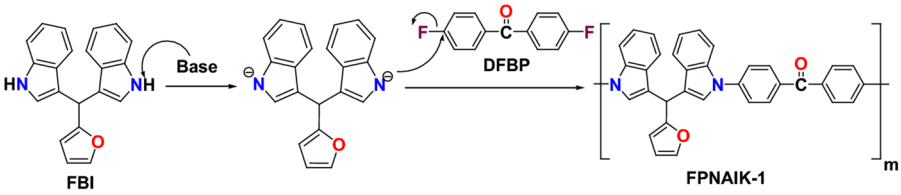
Table 1 Yield and viscosity of (co)poly[(N-arylene diindolylmethane) ketone]s

Polymer[a] Code	Monomers			Observed FBI mol % [b]	Yield %	Inherent viscosity dL/g[c]
	FBI m mol %	DIM n mol%	DFBP m+n mol %			
FPNAIK-1	100	0	100	100	96	0.45
FPNAIK-2	75	25	100	74	95	0.43
FPNAIK-3	50	50	100	50	96	0.42
FPNAIK-4	25	75	100	24	95	0.44
FPNAIK-5	0	100	100	0	95	0.43

[a]Polymerization was carried out with 4 mmol each of 4,4-difluorobenzophenone and bisindoles

[b]The observed mol% of FBI was determined from ^{1}H-NMR spectra (Fig. 2 and S5-S8)

[c]Inherent viscosity was measured at a concentration of 0.5% w/v in NMP at 30 °C



Scheme 3 Mechanism of polymerization of 3,3′-(furan-2-ylmethylene)bis(1H-indole) with 4,4-difluorobenzophenone via C-N coupling process

effect of the N-aryl linkage. A broad multiplet centred at δ 7.60 (8H) corresponds to the protons '$\mathbf{H_b}$' of the two phenyl rings of the benzophenone unit, confirm the presence of the diaryl ketone segment in the polymer backbone. The signal at δ 7.00 (6H) for the remaining aromatic protons '$\mathbf{H_d}$' of the bis-indole rings, verified the integrity of the heteroaromatic framework.

The furan substituent gives three well-resolved resonances: δ 6.36 (1H) corresponds to the C-4 proton '$\mathbf{H_e}$', δ 6.21 (1H) attributed to the C-3 proton '$\mathbf{H_f}$', and δ 7.43 (1H) as discussed for the C-5 proton '$\mathbf{H_c}$'. A resonance at δ 6.06 (1H) is ascribed to the methylene proton '$\mathbf{H_g}$' linking the two indole units; its relatively downfield position arises from deshielding by adjacent aromatic and carbonyl groups, consistent with a conjugated environment. The ^{1}H NMR analysis is consistent with the proposed polymer structure.

^{13}C-NMR of Furyl-(co)poly[(N-arylene diindolylmethane) ketone] FPNAIK-1

The ^{13}C NMR spectrum of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1) bearing a pendant furan ring exhibited distinct resonances consistent with the proposed structure (Fig. 3). The most downfield signal at '$\mathbf{C_a}$' δ 194.28 ppm is assigned to the carbonyl carbon of the benzophenone moiety, confirm the presence of the ketone functionality. The resonance at δ 155.93 ppm corresponds to the furan carbon '$\mathbf{C_b}$' adjacent to oxygen, while signals at δ 143.41 and 141.81 ppm arise from carbons located next to the indole nitrogen '$\mathbf{C_c}$' and furan oxygen '$\mathbf{C_d}$', respectively. The cluster of resonances in the δ 136.12–119.22 ppm range can be attributed to the

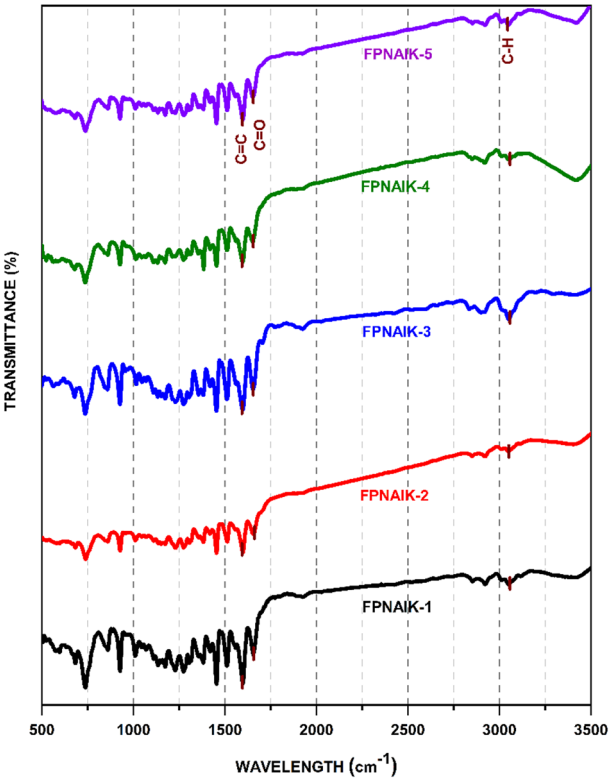


Fig. 1 FT-IR spectra of (co)poly[(N-arylene diindolylmethane) ketone]s

aromatic carbons '$\mathbf{C_{e\text{-}n}}$' of the indole, furan, and the two phenyl rings of the benzophenone group, indicating a high degree of π-conjugation. The signals at δ 110.49 and 107.27 ppm correspond to electron-rich carbons '$\mathbf{C_p}$' and '$\mathbf{C_q}$' of the furan. The signal at δ 110.91 corresponds to electron-rich carbon '$\mathbf{C_o}$' of the indole units. A characteristic upfield resonance at δ 34.12 ppm is ascribed to the methylene '$\mathbf{C_r}$' (-CH_2-) bridge linking the two indole moieties. The ^{13}C NMR spectrum provides evidence for the formation of the (co)poly[(N-arylene diindolylmethane)ketone]s bearing pendant furyl groups.

^{13}C Distortionless Enhancement by Polarization Transfer (DEPT) NMR of FPNAIK-1

The ^{13}C NMR DEPT-135 spectrum (100 MHz, $CDCl_3$) of (co)poly[(N-arylene diindolylmethane) ketone]s bearing a pendant furan ring revealed characteristic signals correspond to the protonated carbon environments (Fig. 4). The resonance at δ 141.69 was assigned to the CH carbon '$\mathbf{C_d}$' adjacent to the oxygen atom of the furan ring. The signals at δ 131.70 and 126.18 correspond to the CH carbons '$\mathbf{C_g}$' and '$\mathbf{C_i}$' of the aromatic rings belonging to the benzophenone moiety. A distinct resonance at δ 123.18 was attributed to the CH carbon '$\mathbf{C_J}$' adjacent to the nitrogen atom of the indole unit. The signals appeared at δ 123.08, 120.90, 120.26, and 110.78, correspond

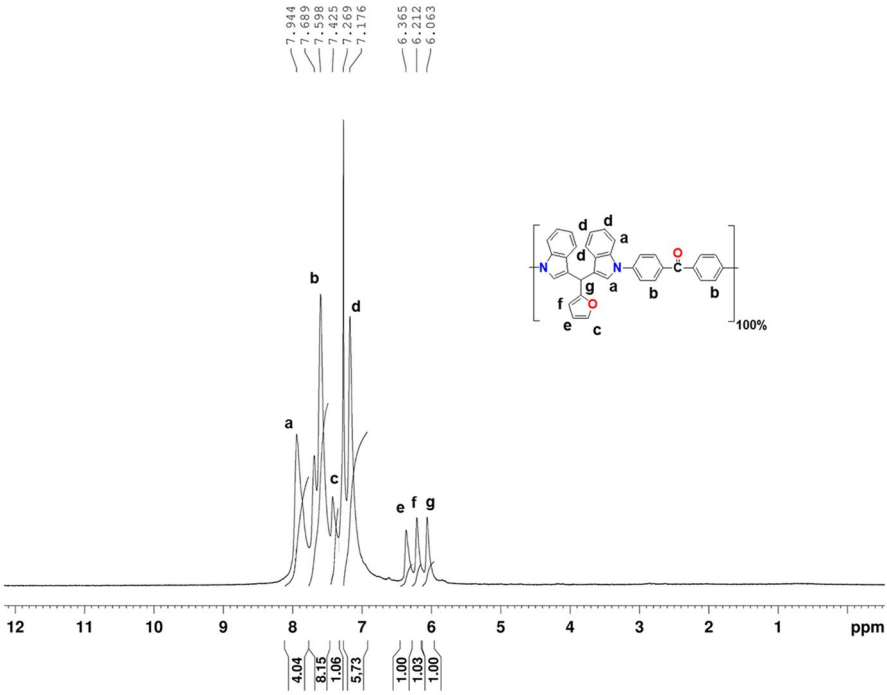


Fig. 2 ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of FPNAIK-1

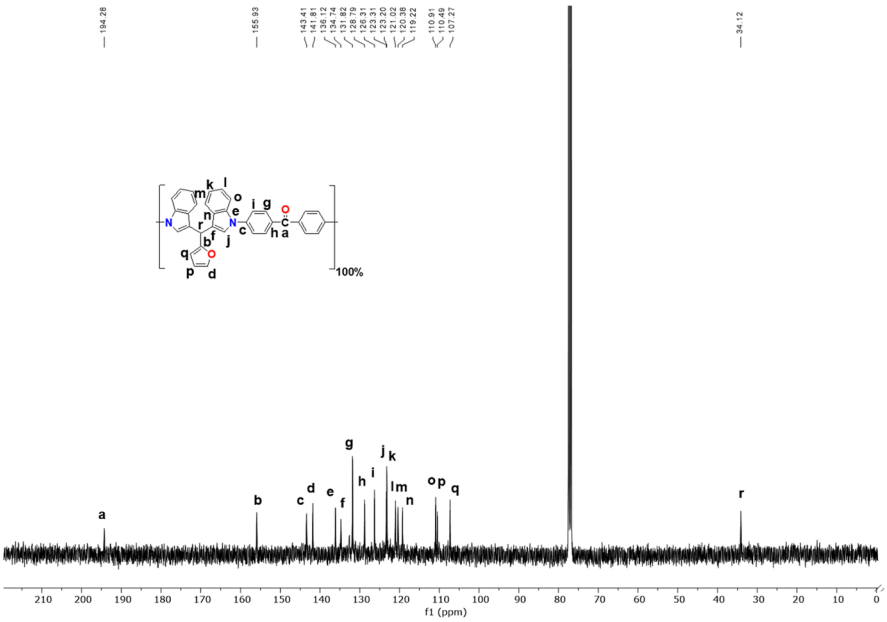


Fig. 3 ^{13}C-NMR (400 MHz, $CDCl_3$) spectrum of FPNAIK-1

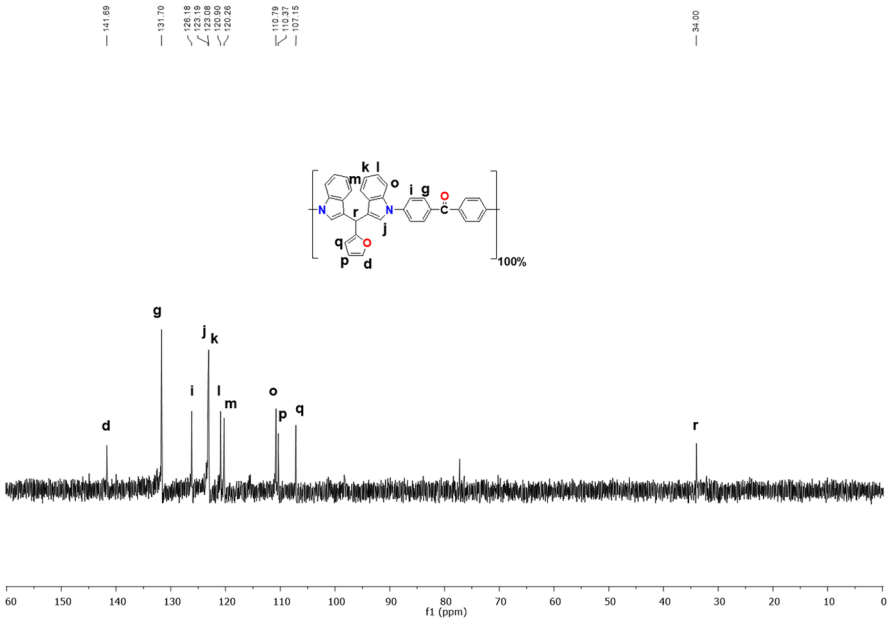


Fig. 4 ^{13}C DEPT-135(100 MHz $CDCl_3$) spectrum of FPNAIK-1

to aromatic CH carbons '$\mathbf{C_k}$', '$\mathbf{C_l}$', '$\mathbf{C_m}$' and '$\mathbf{C_o}$' of the indole, respectively. The CH carbons resonated at δ 110.36 and 107.15, correspond to the electron-rich furan rings carbons '$\mathbf{C_p}$' and '$\mathbf{C_q}$'. In addition, the CH carbon resonated at δ 33.99 was assigned to the methylene carbon '$\mathbf{C_r}$' bridging the bisindole moiety, confirm the -CH- linker.

The DEPT-^{13}C NMR spectrum of FPNAIK-1 showed only positive signals arising from aromatic CH carbons, with no negative peaks, confirming the absence of methylene (CH_2) groups in the polymer structure. The carbonyl resonance '$\mathbf{C_a}$' and the quaternary carbons ($\mathbf{C_b}$, $\mathbf{C_c}$, $\mathbf{C_e}$, $\mathbf{C_f}$, $\mathbf{C_h}$, and $\mathbf{C_n}$) were not visible in the DEPT-135 spectrum, which is consistent with the characteristic suppression of non-protonated carbons. These results obtained by DEPT-135 confirmed the successful synthesis and structural integrity of the FPNAIK-1.

Optoelectronic properties of Furyl-(co)poly[(N-arylene diindolylmethane) ketone] FPNAIK-1

The optoelectronic properties of FPNAIK-1 was assessed through optical and electrochemical measurements (Table 2). In the UV–Vis spectrum (Fig. 5a), a strong absorption peak was observed at 355 nm, with the absorption edge located at 440 nm, corresponds to an optical band gap of 2.82 eV. Photoluminescence analysis (Fig. 5b) showed an excitation feature around 375 nm and emission at 491 nm exhibit weak green emission (Fig. 5c). The Stokes shift between absorption and emission bands indicates charge-transfer interactions and relaxation of the excited state within the donor–acceptor framework.

Table 2 Optoelectronic properties of Furyl-(co)poly[(N-arylene diindolylmethane) ketone]s

Property/Parameter	Value	Technique/Note
UV absorption max (λ_{max})	355 nm	Strong absorption band
Absorption onset (λ_{onset})	440 nm	Determined by the tail absorption method
Optical band gap (E_g)	2.81 eV	$E_g = 1240/\lambda_{onset}$
Photoluminescence excitation	375 nm	Excitation band
Photoluminescence emission	491 nm	Strong emission band
Quantum Yield ϕ_f	1.1%	Fluorescence quantum yield ϕ_f in NMP solution determined using quinine sulfate (0.55 in 1 M H_2SO_4) as standard
Emission colour	Light green	
Oxidation onset (E_{onset})	0.46 V vs Ag/AgCl	From cyclic voltammetry
HOMO level	–5.26 eV	HOMO = E_{onset} + -4.8
LUMO level	–2.44 eV	LUMO = HOMO + E_g

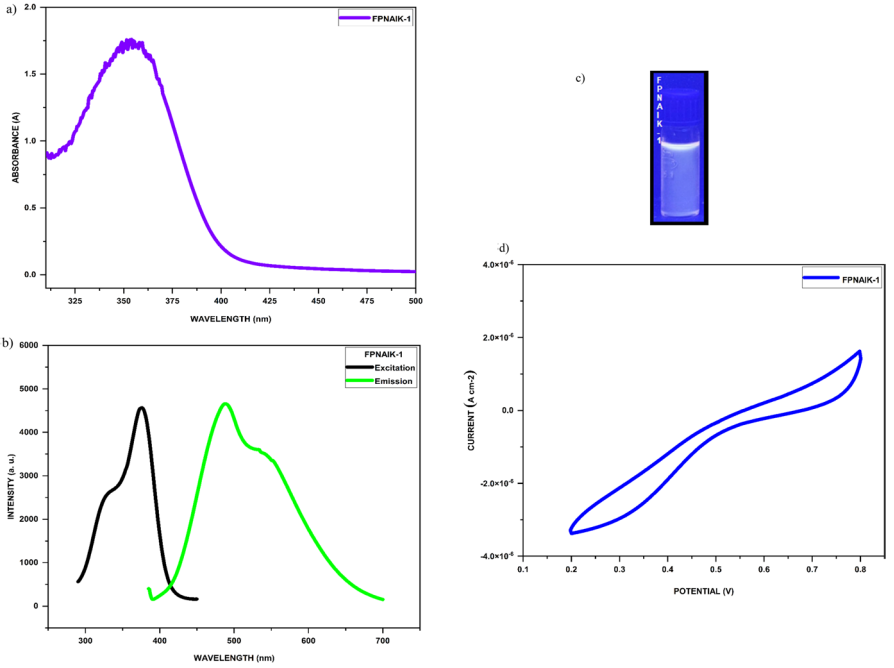


Fig. 5 (**a**) UV and (**b**) Fluorescence spectra of FPNAIK-1 in NMP Solution 10^{-5} M. (**c**) Fluorescence images of FPNAIK-1 in NMP, irradiated at 365 nm. (**d**) Cyclic voltammograms of FPNAIK-1 are conducted in aqueous H_2SO_4 (1.0 M) at a scan rate of 20 mV s^{-1}

Electrochemical analysis using cyclic voltammetry exhibited an oxidation onset at 0.46 V vs. Ag/AgCl, from which the Highest Occupied Molecular Orbital (HOMO) energy level was calculated as -5.26 eV (Fig. 5d). By combining this value with the optical band gap, the Lowest Unoccupied Molecular Orbital (LUMO) was estimated to be -2.44 eV. These highlighted the role of the pendant furan substituent, which enhances π-electron density. At the same time, the indolic nitrogen atoms donate elec-

tron density to stabilise the HOMO, and the electron-withdrawing carbonyl ketone units lower the LUMO. The donor–acceptor balance results in a deep HOMO level, a wide band gap, and weak green luminescence. These properties support further evaluation in Organic Light-Emitting Diodes (OLED), Organic Photovoltaic (OPV), and electron-blocking layer applications.

Thermal properties of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5)

The thermogravimetric analysis (TGA) of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5) confirmed that all members of the series possess high thermal resistance with $T_{d10\%}$ values exceeding 450 °C (Fig. 6). The furyl-functionalised polymers exhibited $T_{d10\%}$ decomposition onsets in the range of 450–460 °C and retained higher char yields (63.6–49.5%) than the non-furyl polymer, the role of the pendant furan group in promotes cross-linking and efficient carbonisation at elevated temperatures. This stabilising effect is related to the indolic nitrogen atoms, which donate electron density and reinforce the backbone, and the electron-withdrawing carbonyl ketone units, which restrict chain scission and enhance structural rigidity.

Although non furyl-FPNAIK-5 shows a slightly delayed degradation onset ($T_{d10\%}$ ≈ 470 °C), its char residue (~42.6%) is lower than the furyl-polymers. This indicates

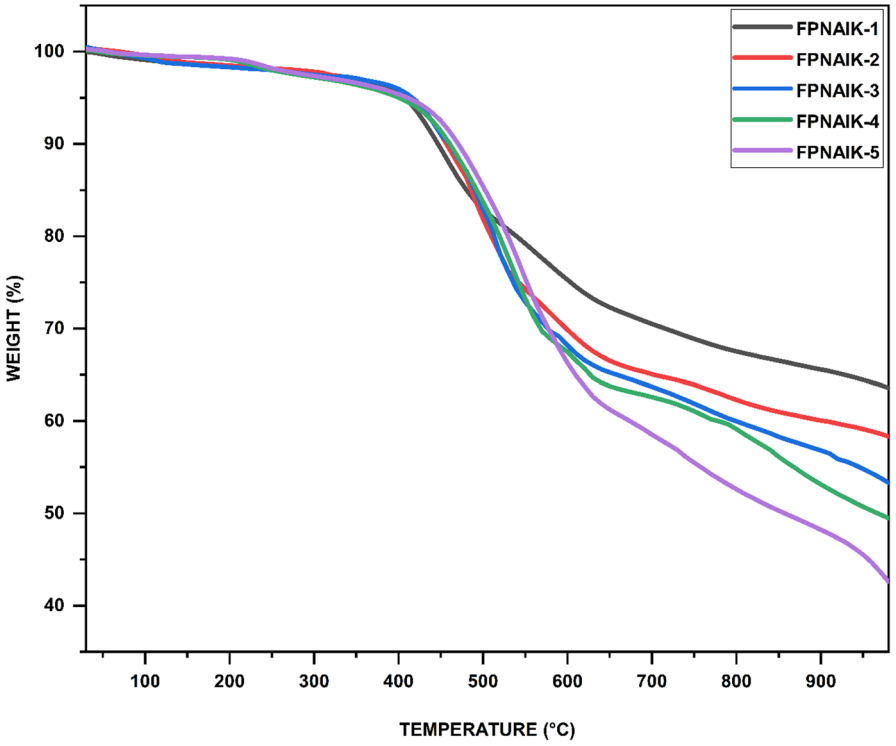


Fig. 6 Thermogravimetric analysis of FPNAIK-1 to 5

that while all polymers demonstrate exceptional onset stability above 450 °C, the furyl derivatives provide a distinct advantage in residual stability and carbon yield These results indicate that the pendant furyl moiety influences carbonization behaviour while maintaining thermal stability. The furyl-containing polymers exhibit characteristics relevant to applications requiring thermal durability.

The differential thermal analysis (DTA) of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1 to 5) show a consistent sequence of thermal events (Fig. 7). A broad endothermic transition above 450 °C marks the onset of backbone decomposition. This is followed by two successive exothermic processes observed in all polymers. The first exotherm appears at ~ 500 °C and is attributed to cross-linking reactions and aromatization of partially degraded chains. The second, more intense exotherm centred near 570 °C corresponds to carbonization and the development of a stable carbonaceous framework. While the positions of these transitions are similar for the series, the furyl-substituted polymers exhibited stronger exothermic intensities, indicating that the pendant furan units participate in high-temperature condensation and structural reorganization processes (Table 3).

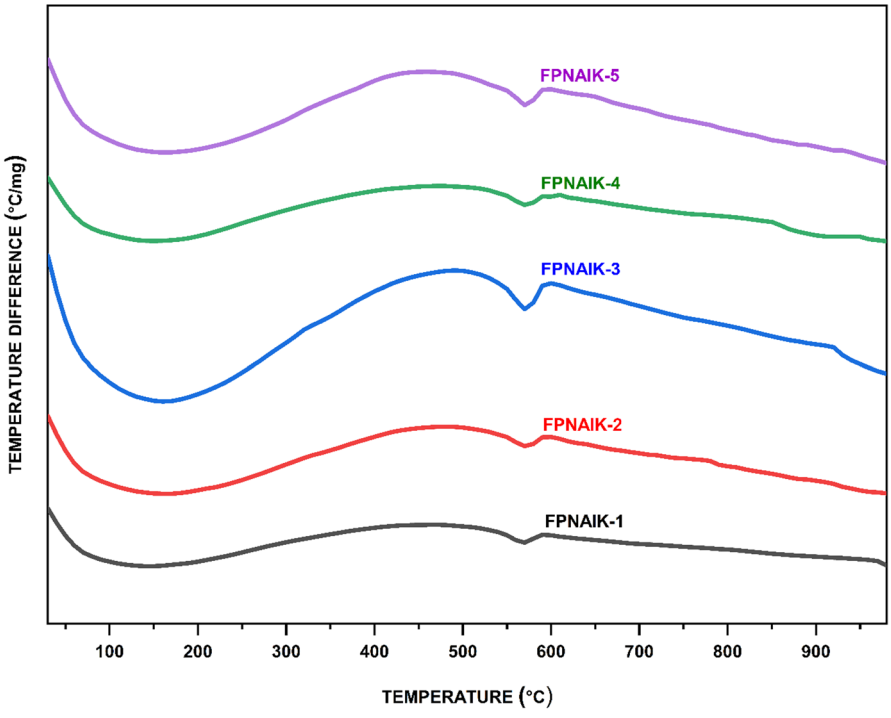


Fig. 7 Differential thermal analysis of FPNAIK-1 to 5

Table 3 Thermal properties of (co)poly[(N-arylene diindolylmethane) ketone]s

Polymer Code	Thermal behaviour				
	T_{d5} °C	T_{d10} °C	1st T_{exo} °C	2nd T_{exo} °C	Residual Wt % at 980 °C
FPNAIK-1	400	450	500	570	63.59
FPNAIK-2	405	460	500	570	58.34
FPNAIK-3	410	460	500	570	53.32
FPNAIK-4	410	460	500	570	49.47
FPNAIK-5	410	470	500	570	42.59

T_{d5}—Temperature of 5% decomposition

T_{d10}—Temperature of 10% decomposition

T_{exo}—Differential thermal analysis temperature determined a heating rate of 10 °C/min

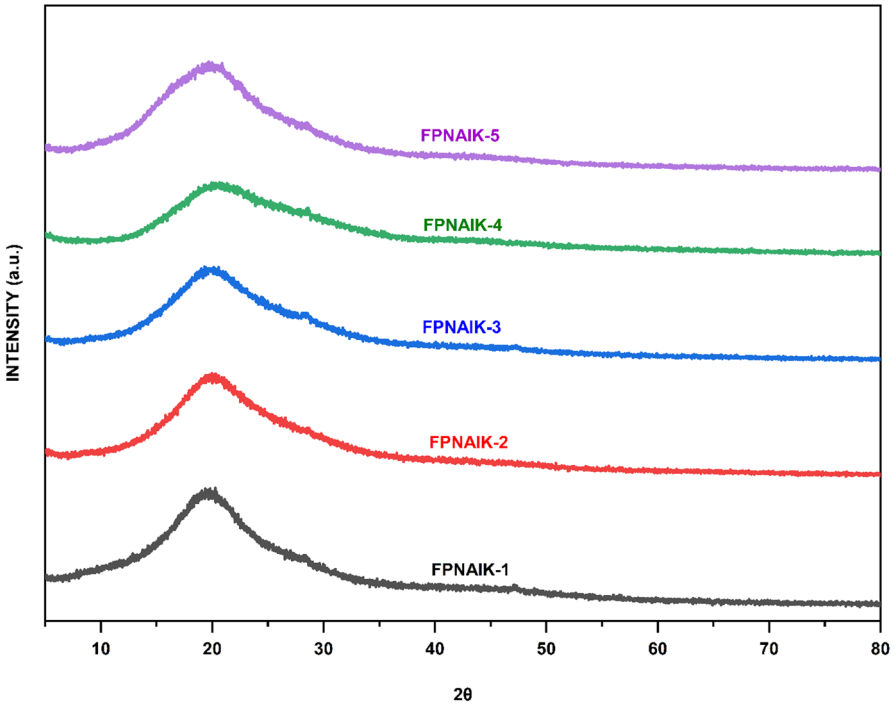


Fig. 8 XRD plot of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5)

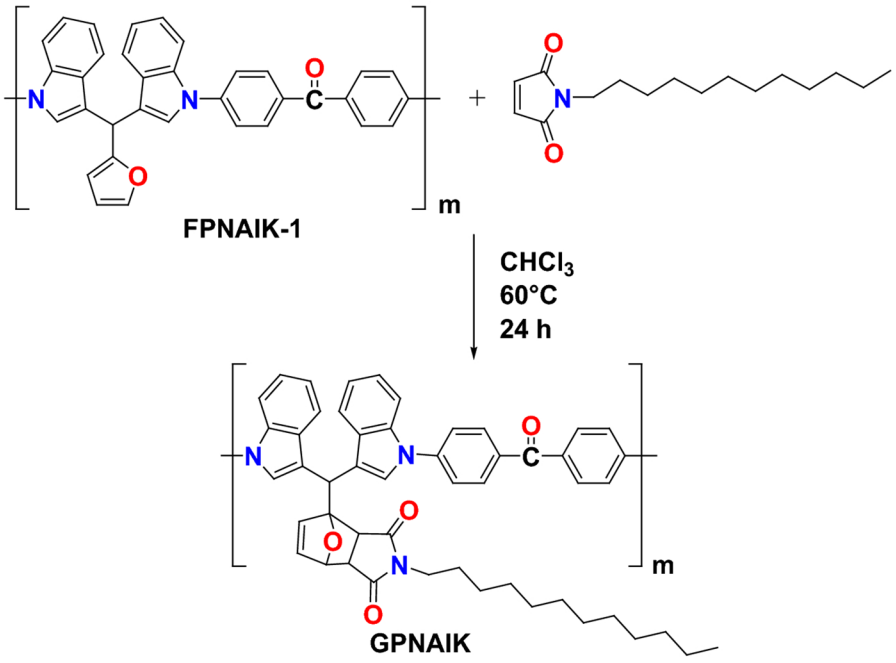
X-ray diffraction studies of (co)poly[(N-arylene diindolylmethane) ketone]s FPNAIK-1–5

The X-ray diffraction (XRD) pattern of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1–5) displayed a broad peak centred at $2\theta \approx 20°$, characteristic of an amorphous polymer (Fig. 8). The absence of sharp crystalline reflections indicates that the polymer chains do not adopt long-range ordered packing, which can be attributed to the presence of the rigid indole, pendant furan ring, ketone functionalities,

and n-arylene linkage that hinders crystallization. This amorphous morphology is a feature of high-performance heteroaromatic polymers, where bulky substituents and irregular backbone conformations restrict molecular ordering. The XRD data provide evidence of the disordered structural arrangement in FPNAIK, consistent with its polymeric framework and functional design.

Synthesis of post-modified (co)poly[(N-arylene diindolylmethane) ketone]s (GPNAIK)

The post-modification of (co)poly[(N-arylene diindolylmethane) ketone]s bearing pendant furan ring (FPNAIK-1) with N-dodecylmaleimide proceeded through a Diels–Alder cycloaddition. The electron-rich furan moieties in the polymer backbone reacted with the electron-deficient maleimide double bond (Scheme 4). This reaction successfully introduced long aliphatic dodecyl side chains as flexible pendant groups along the rigid aromatic framework. This resulted in disruption of dense molecular packing and weakening of π-π interactions, which increased the free volume within the polymer matrix. The Diels–Alder reaction as a post-polymerization strategy for introducing aliphatic side chains, which improved the solubility and processability of FPNAIK.



Scheme 4 Synthesis of post-modified (co)poly[(N-arylene diindolylmethane) ketone]s GPNAIK

FT-IR of post-modified (co)poly[(N-arylene diindolylmethane) ketone]s

Fourier transform infrared (FTIR) spectroscopy confirmed the successful transformation of functional groups from FPNAIKs into post-modified GPNAIKs (Fig. 9). The post-modified polymer exhibited a strong absorption band at 1701 cm^{-1} corresponding to the imide carbonyl group, along with a distinct band at 1656 cm^{-1} attributable to the ketone carbonyl of the FPNAIK backbone. The presence of both carbonyl bands is consistent with the incorporation of maleimide units without alteration of the ketonic structure of the parent polymer.

^{1}H-NMR of post-modified (co)poly[(N-arylene diindolylmethane) ketone]s (GPNAIK)

The ^{1}H NMR spectrum of GPNAIK is consistent with the expected polymer structure. Characteristic resonances of the indole-furyl-biphenyl backbone, the bisindole linkage, and the Diels–Alder-derived maleimide units were observed (Fig. 10). In the aromatic region (δ 7.9–6.0 ppm), the most downfield signal (δ ≈ 7.9 ppm) is assigned to the indole proton '$\mathbf{H_a}$' deshielded by the adjacent heteroatoms. Multiplets at δ 7.7–7.3 ppm arise from the biphenyl aromatic protons '$\mathbf{H_b}$', while the δ 7.3–6.9 ppm correspond to the remaining indole proton '$\mathbf{H_d}$'. At δ ≈ 6.6 ppm the bridging methine

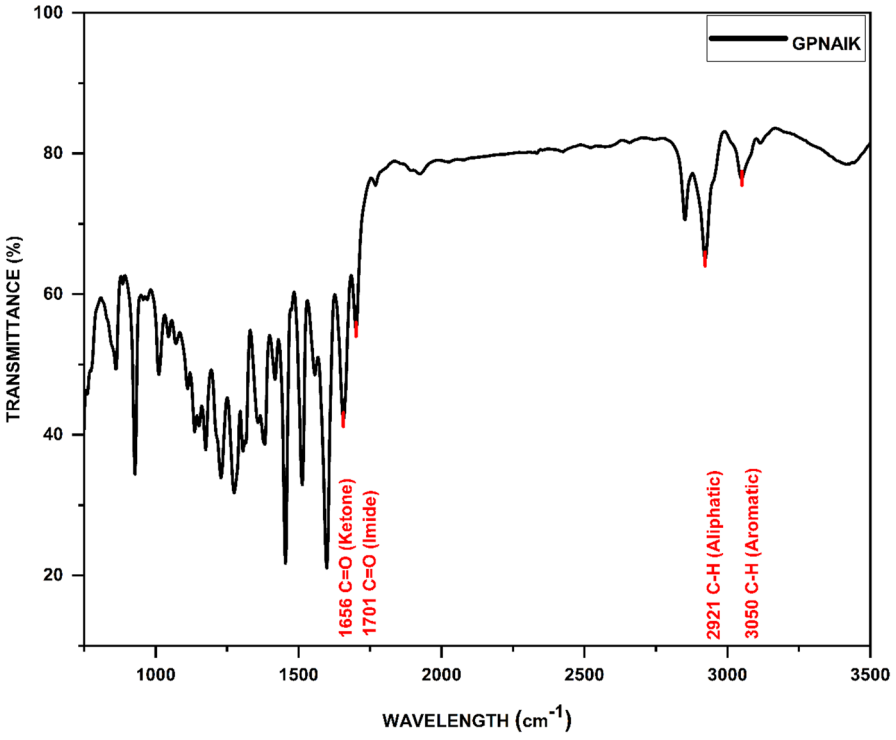


Fig. 9 FT-IR spectrum of GPNAIK

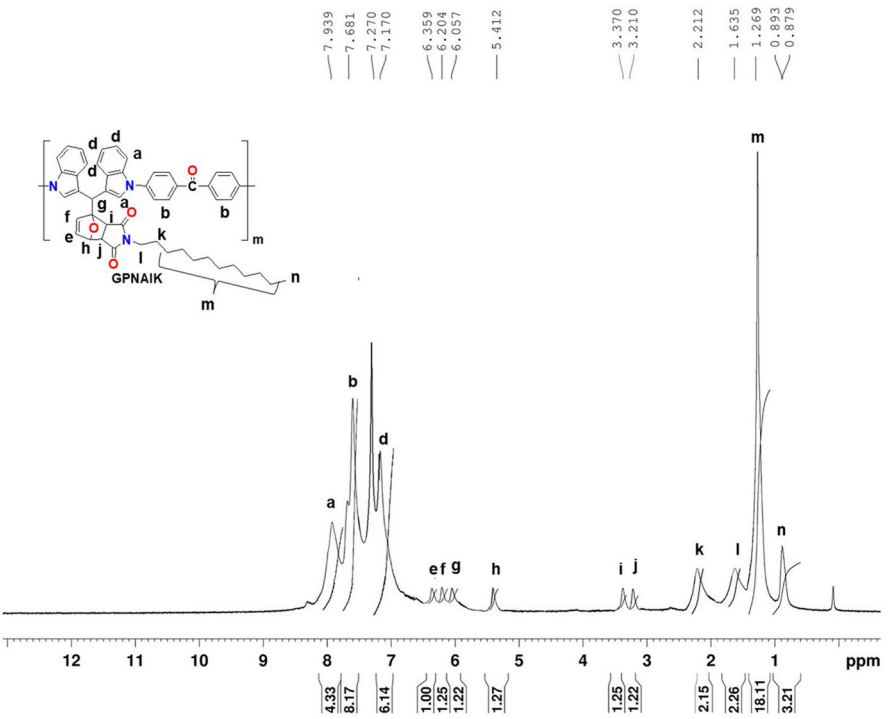


Fig. 10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of GPNAIK

'$\mathbf{H_g}$' of the bisindole linkage is observed, confirming bisindole connectivity within the backbone. Additional aromatic resonances between δ 7.0–6.1 ppm are attributed to the furyl ring protons '$\mathbf{H_e}$' and '$\mathbf{H_f}$'. A diagnostically shifted signal at δ 5.4 ppm is assigned to the proton '$\mathbf{H_h}$' adjacent to the oxygen atom of the furyl moiety in the Diels–Alder adduct, its downfield position reflecting the combined effects of the electronegative oxygen and conjugation in the adduct.

The aliphatic region similarly supports the structural model: signals at δ 3.4 and 2.2 ppm are attributed to protons '$\mathbf{H_i}$' and '$\mathbf{H_j}$' on the maleimide ring introduced by the Diels–Alder reaction, while the resonances at δ 2.3 and 1.8 ppm correspond to methylene groups '$\mathbf{H_k}$', '$\mathbf{H_l}$' directly adjacent to the maleimide nitrogen (N-CH_2 and the succeeding CH_2), consistent with an N-linked alkyl spacer from the maleimide adduct. The broad, intense multiplet at δ 1.6–1.2 ppm represents the bulk methylene envelope of the long alkyl substituent '$\mathbf{H_m}$', and at δ ≈ 0.9 ppm corresponds to the terminal methyl protons '$\mathbf{H_n}$'. The ^{1}H NMR data support the post-modified polymer structure.

XRD of post-modified (co)poly[(N-arylene diindolylmethane) ketone]s (GPNAIK)

The crystallinity of GPNAIKs was analyzed by X-ray Diffraction Techniques (Fig. 11). The XRD pattern displayed a broad halo centered at ~ 20° (2θ), characteristic of an amorphous material. The absence of sharp crystalline peaks indicates

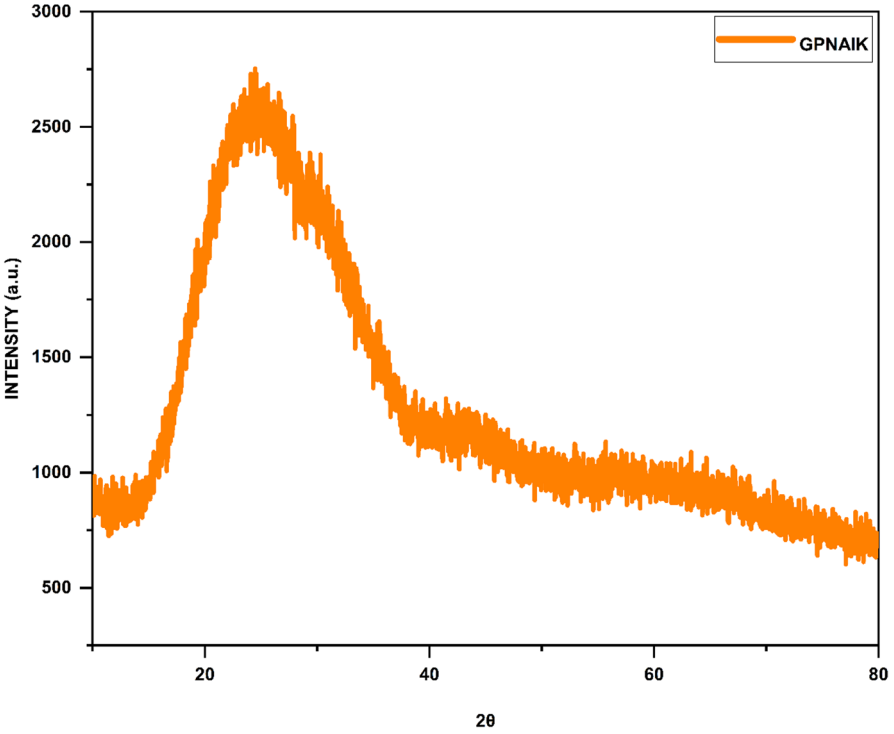


Fig. 11 XRD plot of GPNAIK

Table 4 Solubility of (co) poly[(N-arylene diindolylmethane) ketone]s

Solvent	FPNAIK-5 (Non-furyl)	FPNAIK-1 (Furyl)	Post-modified GPNAIK
Chloroform	Δ+	+	+
THF	Δ+	Δ+	+
Toluene	-	-	-
DMF	Δ+	Δ+	+
DMSO	Δ+	+	+
NMP	+	+	+
DMAc	Δ+	Δ+	+
Acetone	-	-	-
Methanol	-	-	-
Conc. H_2SO_4	+	+	+

(-): Insoluble, (Δ+): Soluble on Heating, (+): Soluble at rt.

disruption of regular chain packing, which can be attributed to the incorporation of bulky and flexible dodecyl substituents.

Solubility

A systematic solubility evaluation of non-furyl FPNAIK-5, furyl-FPNAIK-1, and the post-modified FPNAIK revealed differences in solvent compatibility (Table 4).

The parent Non-furyl FPNAIK-5 exhibited poor solubility in most organic solvents; it was insoluble in toluene, acetone, and methanol. Non-furyl FPNAIK-5 is soluble upon heating in highly polar aprotic solvents such as chloroform, THF, DMF, DMSO, and DMAc. Solubility at room temperature was observed in NMP and concentrated H_2SO_4, consistent with the behaviour of rigid, highly conjugated aromatic polymers.

The introduction of pendant furyl group in polymers slightly enhanced solubility. FPNAIK-1 dissolved in chloroform, DMSO, NMP, and conc. H_2SO_4 at room temperature, while showing poor solubility in THF, DMF and DMAc, that improved upon heating. However, it remained insoluble in toluene, acetone, and methanol.

The post-modified GPNAIK, bearing flexible dodecyl side chains introduced via *N*-dodecylmaleimide through a Diels–Alder reaction, exhibited enhanced solubility across a broad range of solvents. It was soluble in chloroform, THF, DMF, DMSO, NMP, DMAc, and conc. H_2SO_4 at room temperature.

These results demonstrate that post-modification disrupts interchain packing and reduces strong intermolecular interactions, improving chain mobility and processability. The improved solubility of the post-modified polymer GPNAIK enables solution processing and film formation.

Conclusion

In summary, the 3,3′-(furan-2-ylmethylene)bis(1H-indole) (FBI) monomer was synthesized from renewable furfural and indole. The FBI monomer was polymerized with 4,4′-difluorobenzophenone and 3,3′-diindolylmethane via C-N coupling to obtain a series of (co)poly[(N-arylene diindolylmethane) ketone]s (FPNAIK-1 to 5). The polymers exhibited inherent viscosities of 0.42–0.45 dL g^{-1}, indicates moderate molecular weights. Thermogravimetric analysis under nitrogen showed thermal stability with Td_{10} values above 450 °C. UV–visible spectroscopy of FPNAIK-1 revealed an absorption maximum at 355 nm, consistent with the conjugated backbone. Fluorescence measurements showed weak green emission in solution, attributed to π–π* transitions. Cyclic voltammetry exhibited quasi-reversible oxidation–reduction responses, indicating stable electroactive behaviour. X-ray diffraction displayed broad halos without sharp peaks, confirmed the amorphous nature of the polymers.

Post-modification of FPNAIK-1 bearing a pendant furan ring with *N*-dodecylmaleimide through a Diels–Alder reaction resulted in the incorporation of aliphatic side chains to the polymer backbone. This post-modification improved solubility and processability without altering the backbone structure. The study includes furfural-based polymer synthesis, post-modification and optoelectronic properties. Device fabrication, charge-transport evaluation, long-term stability testing, and scalability assessment will be addressed in future studies to evaluate performance under practical operating conditions for optoelectronic applications.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00289-026-06404-7.

Acknowledgements The authors gratefully acknowledge the Government of Maharashtra for providing Ph.D. research fellowship support through the Mahatma Jyotiba Phule Research and Training Institute (MJPRI), Nagpur, India [Fellowship No. fellowship2022_1926].

Author contributions Suraj D. Jadhav: Conceptualization, Methodology, Investigation, Writing-Original Draft, Writing-Review & Editing. Pradip Chavan: Data Curation, Software, Formal Analysis. Anil A. Ghanwat: Resources, Review. Sanjay S. Ankushrao: Supervision, Validation, Visualization, Formal Analysis, Resources.

Data availability The data that support the findings of this study are available in the supplementary material of this article.

Declarations

Conflict of interest The authors declare no competing interests.

Financial interest The authors declare that they have no financial interest.

Consent for publication All authors agree to publish this research work.

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