



Cyanopyridine based conjugated polymer-synthesis and characterization



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ABSTRACT

Two novel D-A polymers containing pyridine with vinylene spacer, **P1** and **P2** were synthesised through Heck polymerisation. In both the polymers, pyridine is linked with two donor phenylene at position-4 and -6, and electron withdrawing cyano group at position-3. Additionally, **P1** possess *methoxy* side chain at position-2 of 3-cyanopyridine and **P2** is flanked with both *methoxy* and *octyloxy* side chain at alternate pyridine. The polymers are well characterised with ¹H-NMR, UV–Vis absorption, PL, GPC, TGA, cyclic voltammetry and AFM. TGA data reveal that the polymers **P1** and **P2** are thermally stable up to 350–400 °C. The UV–Vis absorption spectra for solid thin films envisage efficient molecular stacking with red shifting the absorption maxima to 30 nm when compared to solution. The obtained polymers have a band gap of 1.8–1.93 eV with low lying HOMO and LUMO energy level. The polymers displayed very good blue fluorescence in CHCl₃ upon irradiated with UV light (254 nm) and Atomic force microscopy (AFM) applications to polymer **P1** and **P2** surfaces are providing interesting images of nanometre-scale polymer structures.

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1. Introduction

With ever increasing demand for clean energy, the need to develop new technology to harness renewable energy has become very important. In this aspect, polymer solar cells (PSCs) and electroluminescence have been extensively researched due to their inherent advantages viz., ease of processibility, flexibility and cost effectiveness [1–3]. PSCs also have the advantage of tunability of electronic property with regard to the donor and acceptor unit in the polymer leading to extension in the absorption range of solar spectrum [4,5]. Polymers with narrow band gap are highly crucial for the performance of the PSC [6,7] and this can be successfully achieved with molecular designing of the polymer having an electron rich donor (D) and electron deficient acceptor (A) which facilitates intra-molecular charge transfer (ICT) [8–13]. Further, introduction of π -spacers enables the stacking of the polymer chain

facilitating intermolecular charge transfer [14,15].

Pyridine is a known electron deficient molecule and it is used as an acceptor owing to its very good electron withdrawing property [16]. Generally, low lying lowest unoccupied molecular orbital (LUMO) reduces the environmental oxidation of the polymer leading to a stable polymer [17]. Hence, the quest for new polymeric designs to reduce both the highest occupied molecular orbital (HOMO) and LUMO is essential. Further, the presence of electron withdrawing cyano group in the polymer reduces both HOMO and LUMO energy level, thus facilitates higher open circuit voltage (V_{OC}) [18,19]. Cyano group also facilitates the self-assembly of the polymer leading to a better morphology [19]. Seri et al. synthesised pyridine based polymer with vinylene spacer containing 3,4-ethylenedioxythiophene as donor moiety but found that the polymer obtained is having lower molecular weight and less solubility [20]. It has been reported that the presence of vinylene spacer reduces the band gap [21–24], increases charge transfer with increased self-assembly [25,26] and also enhances the delocalisation of the electron leading to increased π conjugation than compared to the simple D-A copolymers.

On this premises, we have designed a cyanopyridine acceptor

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with enhanced electron withdrawing capacity thus to lower the HOMO and LUMO. Two D-A-D copolymers were synthesised with two arylene as donor and 3-cyanopyridine as acceptor. Further, the repeating D-A-D units are linked with vinylene spacer to extend the π -conjugation in the polymer main chain. The polymer **P1** carries *methoxy* side chain as substituent at position-2 of pyridine, whereas, **P2** bears the alternating *methoxy* as well as *octyloxy* side chain as substituents at position-2 of pyridine (Scheme 1). The present design is intended to facilitate the intramolecular charge transfer and flanking different side chain is to enable polymer processibility. The copolymers were synthesised with Heck polymerisation technique with very narrow polydispersity index.

The pyridine is linked at *ortho* and *para* positions with the phenylene donor. Pyridine is an electron deficient and the resonance structure of the pyridine creates electron deficiency at *ortho* and *para* site of the pyridine. The resonance will be stabilised with the linking at *ortho* and *para* position of pyridine with phenylene donor and the resonance as shown in Scheme 2. This structure allows effective conjugation and leads to intramolecular charge transfer (ICT) [20]. Together with this, the availability of non-bonding electron on the nitrogen allows the $n \rightarrow \pi^*$ transition and can also facilitate intersystem crossing (ISC) [17]. These criterion makes the pyridine-based polymer a good candidate for light emitting material.

2. Experimental section

2.1. Materials

The reagents and organic solvents were procured from Spectrochem, and used as received without much purification. Compound **2** and **3** were procured from Spectrochem and Compound **1** was synthesised according to the literature [27].

2.2. Instrumentation

IR spectra were collected using Bruker ALPHA eco-ATRIR on ZnSe crystal, UV–Vis spectra were obtained using a Shimadzu UV-1800 spectrophotometer and photoluminescence spectra were collected with Shimadzu RF-5301PC. The $^1\text{H-NMR}$ spectra were collected on a Jeol AV-III400 (L) spectrometer with TMS as reference and deuterated chloroform (CDCl_3) or $\text{DMSO-}d_6$ as solvents operating at 400 MHz. Mass spectra were recorded with Turbo Ion spray (ESI), AB Sciex/API 4000 instrument with samples dissolved in DMSO and diluted with Methanol. Melting point of the monomers and intermediate compounds were estimated with differential scanning calorimetric (DSC) analysis using DSC 851 (Mettler Toledo) under a nitrogen atmosphere at heating rates of $10\text{ }^\circ\text{C min}^{-1}$. The stability of the polymer were analysed with thermo gravimetric analysis using Mettler Toledo TGA/SDTA851e instrument. Cyclic voltammetry (CV) measurements for the polymers were carried out with CHI660D potentiostat CH instrument using an Ag/AgNO_3 as reference electrode, a Pt wire as counter electrode and a glassy carbon as working electrode in

tetrabutylammoniumhexafluorophosphate as electrolyte (TBAPF_6) solution (0.1 M) in acetonitrile. Ferrocene/ferrocenium redox couple (Fc/Fc^+) was used as external calibration reference. The molecular weight and polydispersity index were analysed by gel permeation chromatography (GPC) on Agilent 1260 Infinity system at $30\text{ }^\circ\text{C}$ with anhydrous tetrahydrofuran (THF) as eluent and polystyrene as the reference standard. Atomic force microscopy (AFM) imaging was performed under dry conditions at room temperature ($22 \pm 2\text{ }^\circ\text{C}$) using MultiMode 8 AFM equipped with NanoScope V controller (Bruker, Santa Barbara, CA, USA). Si cantilevers (NSG 01, NT-MDT) with a typical radius of curvature of approximately 10 nm were used. The force constants of AFM probe in the range of 2.5–10 N/m and with resonance frequency in the range of 120–180 kHz. The scan rate used was 1 Hz. The samples for AFM measurements were prepared by drop-casting $30\text{ }\mu\text{L}$ of MST samples onto a freshly cleaved mica sheet and dried overnight under vacuum. Raw data were processed offline using Bruker's NanoScope Analysis software. Surface roughness was reported both in average roughness values.

2.3. Synthesis of monomers and polymers

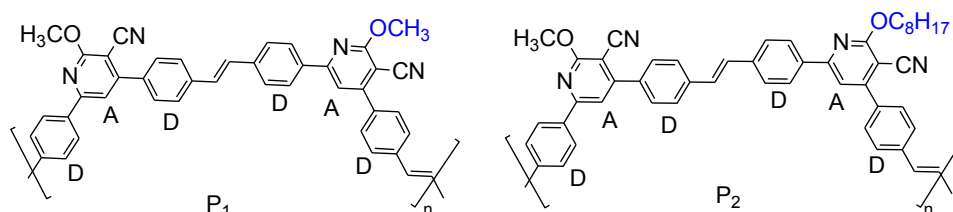
Synthesis of monomers are as shown in Scheme 3. Polymers are synthesised via Heck reaction and are shown in Scheme 4. The detailed synthesis of monomers and copolymers are described as follows.

2.4. 1,3-Bis(4-bromophenyl)prop-2-en-1-one (4)

Compound **2**, 4-bromobenzaldehyde (2 g, 10.8 mmol) and compound **3**, 4-bromoacetophenone (2.15 g, 10.8 mmol) were dissolved in 15 mL ethanol. Aqueous solution of potassium hydroxide (3.24 mmol) was added with constant stirring, and kept the reaction on for 8 h. The obtained precipitate was filtered and washed with 10 mL ethanol and recrystallized from 1:1 ratio of ethanol and chloroform mixture to obtain a pale yellow product **4** (3.722 g, 94%). Melting point, $T_m = 186.57\text{ }^\circ\text{C}$. ATR-IR (cm^{-1}): 810, 998, 1180, 1595, 1654. $^1\text{H NMR}$ (400 MHz, CDCl_3 , d/ppm): 7.43 (s, 1H), 7.49 (d, $J = 1.6\text{ Hz}$, 1H), 7.51 (d, $J = 2\text{ Hz}$, 1H), 7.55 (d, $J = 2\text{ Hz}$, 1H), 7.57 (d, $J = 2\text{ Hz}$, 1H), 7.64 (d, $J = 2\text{ Hz}$, 1H), 7.66 (d, $J = 2\text{ Hz}$, 1H), 7.72 (s, 1H), 7.88 (d, $J = 2\text{ Hz}$, 1H), 7.89 (d, $J = 2\text{ Hz}$, 1H). ESI-MS/MS ($\text{C}_{15}\text{H}_{10}\text{Br}_2\text{O}$), $[\text{M}+\text{Na}]^+$: calcd, 389.05; found, 389.2.

2.5. 4,6-Bis(4-bromophenyl)-2-hydroxypyridine-3-carbonitrile (5)

Compound **2**, 4-bromobenzaldehyde (2 g, 10.8 mmol) and compound **3**, 4-bromoacetophenone (2.15 g, 10.8 mmol) were dissolved in 35 mL of 1,4-dioxane. Ammonium acetate (6.6 g, 85.7 mmol) was added followed with 1.5 mL of ethyl cyanoacetate (12.9 mmol) with constant stirring and kept the reaction at $80\text{ }^\circ\text{C}$ for 24 h. The reaction mixture was cooled and poured into 100 mL of distilled water and stirred for 10 min. The obtained precipitate was filtered and the filtrate was thoroughly washed with 1,4-dioxane and dried to afford a white product **5** (1.66 g, 36%).



Scheme 1. Structure of polymers **P1** and **P2**.

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