

Facile synthesis of urea containing thiophene monomer and its application in the field of D-A conjugated polymer

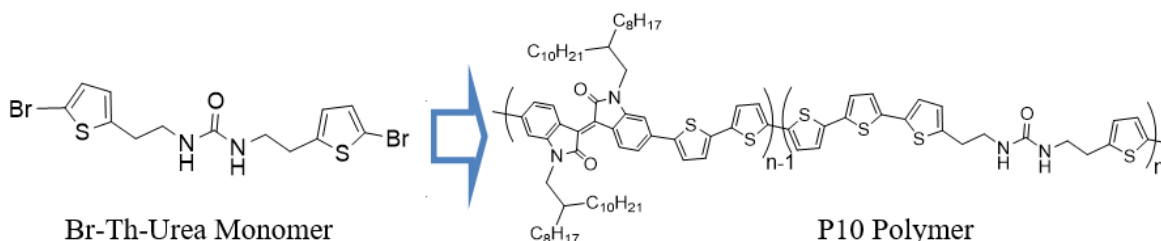
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Article

ABSTRACT



Conjugation Break Spacer “CBS” methodology has proved to be an efficient tool to introduce the flexibility and stretchability into the otherwise known rigid polymeric backbone. CBS monomers with H-bonding unit are widely used in conjugated polymer to make electronic device intrinsically stretchable and self-healable. However, dealing with strong h-bonding system like urea, it is always associated with an uphill task of purification of monomer in each step. Here, we report an efficient method of purification of urea based thiophene monomer in both of its synthetic steps into a single crystal and its application as CBS in the i-indigo D-A conjugated polymer.

Keywords: Conjugation Break Spacer “CBS” Monomers, D-A conjugated polymers, H-Bonding, Urea group

INTRODUCTION

Over the past four decades, π -conjugated semiconducting polymers have attracted significant attention from both academic and industrial laboratories due to a wealth of potential applications in optoelectronic devices. Recently, the progress in achieving high performance of these polymers make them a strong candidate for future application in the field of energy. The areas like organic light-emitting diodes,¹ field effect transistors,² photovoltaics,³ and bioelectronics⁴ are of particular interest. To achieve the level of commercial success certain modifications are required to obtain desired properties of the polymers. This thrust in the field leads to the formation of vast library of literature available to work with.^{5,6}

Generally, π -conjugated polymers have semi-rigid backbone and flexible solubilising side chains. The collective effect of these leads to the formation of different phases in solid state thin

film morphology which dictates the device performance.^{7,8} One such factor is introduction of non-conjugated flexible linkers typically alkyl chain in the polymeric backbone. As the introduction of the linker leads to the disruption of continuous conjugation, the spacers are often referred to as “conjugation-break spacers.” (CBS)⁹⁻¹² Since the linker also add a degree of conformational freedom to the rigid conjugated backbone, they have also been referred to as “flexible linkers.” Initially it was expected to disrupt intramolecular charge carrier transport and create a high degree disorder in the material in the solid state but recent reports demonstrate the usefulness of this approach in providing softer backbone, unique processability and self-assembly to provide greater device performance.¹³⁻²² Instead of using simple alkyl linker, one can think of introducing H-bonding unit. Bao and co-worker have demonstrated the use of H-bonding unit not only shows improved micro-structure of polymer thin film but also intrinsically stretchable semiconducting device supplemented with self-healing properties.²³

Thus, the use of small molecule monomers containing H-bonding unit and flexible alkyl linker has attracted particular attention. For successful synthesis of semiconducting polymers, it is advised to have monomers in purest form. However, dealing with hydrogen bonding system, it is always difficult to purify these molecules. Herein, we report the synthesis thiophene containing urea monomer which potentially been used as non-

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conjugated flexible linker in the *iso*-Indigo based D-A conjugated polymeric backbone. We were able to purify both final monomer and intermediate molecules by crystallising them without going through the tedious separation procedure. The structure of monomer and polymers is shown in figure 1.

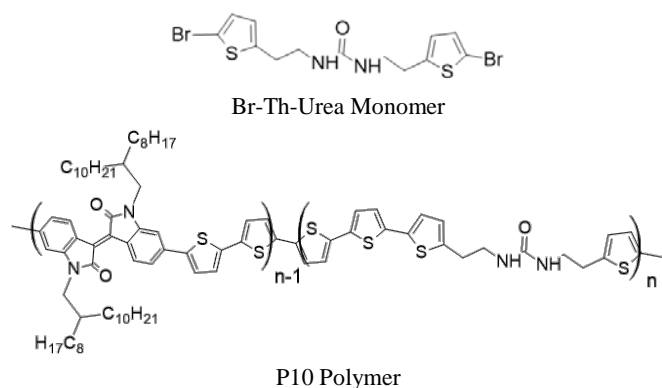


Figure 1: Structure of Monomer and Polymer

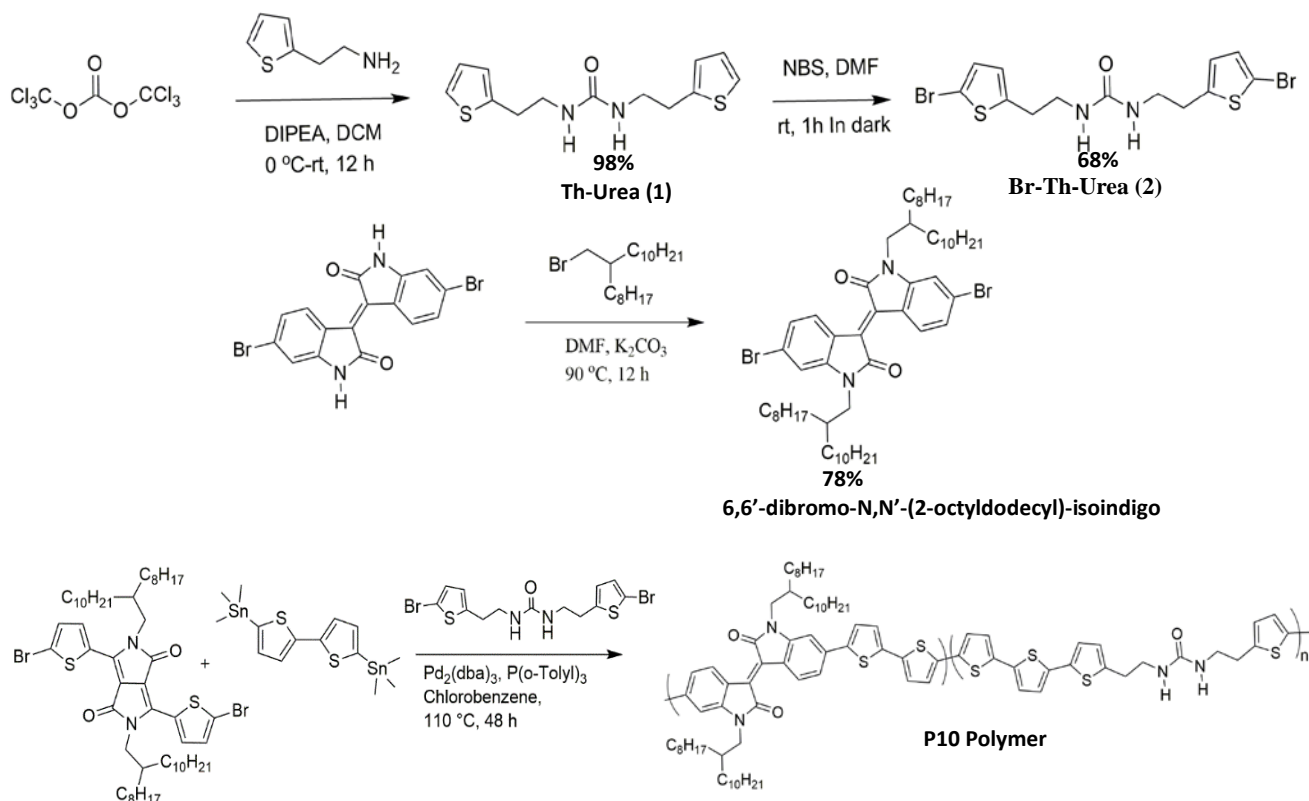
MATERIAL AND SYNTHESIS

Unless otherwise stated, all the chemicals and reagents were obtained commercially and used without further purification. Triphosgene, 2-thiopheneethylamine, N-bromosuccinamide, 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene were purchased from Sigma Aldrich and used as received. 6-bromo Indoline-2,3-dione and 6-bromo indolin-2-one were purchased from TCI Chemicals.

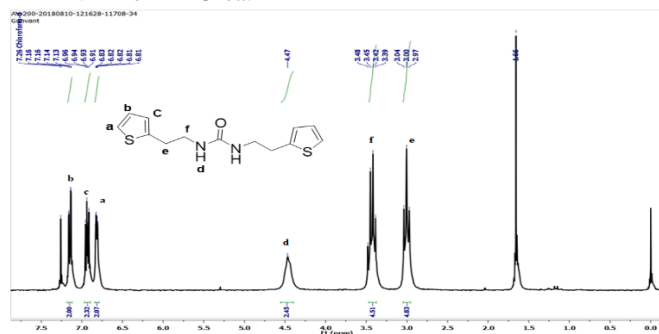
Potassium carbonate was used after drying in oven for overnight. All the solvents were purchased from Merck Chemicals. Analytical Thin Layer Chromatography was done on pre-coated silica gel plates (Kieselgel 60F254, Merck). Column chromatographic purifications were done with 60-120 mesh sized silica gel. All the ^1H NMR spectra were recorded in CDCl_3 on Bruker arx AV 200 MHz and AV 400 MHz Bruker AVANS spectrometer. High temperature ^1H NMR spectra were recorded in 1,1,2,2 tetrachloroethane- d_2 on Bruker arx AV 400 MHz. ^{13}C NMR spectra were measured on Bruker arx 100 MHz AVANS spectrometer.

SYNTHESIS

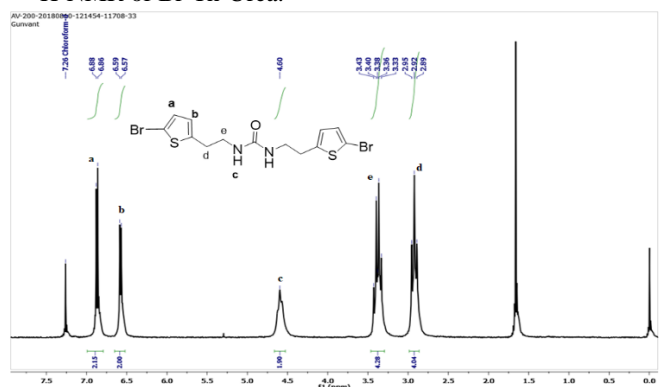
Synthesis of Th-Urea: 200 ml round bottom flask equipped with magnetic stirrer was charged with 2-thiopheneethylamine (5.20 ml; 40.95 mmol) and diethylpropylamine (5.98 ml; 49.05 mmol) dissolved in 50 ml dry Dichloromethane (DCM) at 0°C under argon atmosphere. Triphosgene (2g; 6.82 mmol) dissolved in DCM was added very slowly with the help of syringe through septum over a period of 30 minutes. Resulting mixture was allowed to stir at room temperature for 12 h. The reaction mixture was precipitate in ethyl acetate. Resultant precipitate was washed several times with ethyl acetate to get white color crystalline Th-Urea Monomer (3 g, yield 98%) ^1H NMR (200 MHz, CDCl_3) δ 7.15 (dd, $J = 5.1, 1.2$ Hz, 2H), 6.93 (dd, $J = 5.1, 3.4$ Hz, 2H), 6.85 – 6.79 (m, 2H), 4.47 (s, 2H), 3.43 (dd, $J = 12.7, 6.4$ Hz, 4H), 3.00 (t, $J = 6.5$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.92, 141.77, 127.16, 125.47, 123.99, 77.48, 77.16, 77.16, 76.84, 41.93, 30.77.



Scheme 1: Synthesis of Br-Th-Urea (2) and Polymer P5

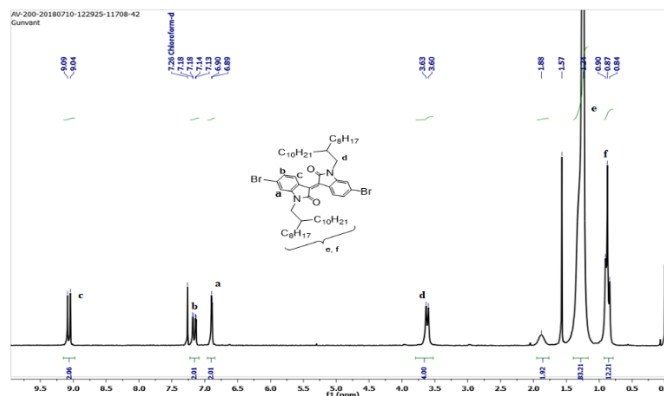
¹H-NMR of Th-Urea:**Synthesis of Br- Th-Urea:**

In 100 ml round bottom flask, Compound B (2 g, 7.14 mmol) was dissolved in 50 ml of DMF at rt under argon atmosphere. The flask was covered with aluminium foil to maintain dark condition. N-Bromo succinimide (1.52 g, 8.57 mmol) was added portion wise over a period of 30 minutes in dark under argon atmosphere. The resulting mixture was stirred at room temperature for 4h. The reaction was monitored by TLC. The reaction was quenched by adding warm water to the reaction mixture and washed twice with the chloroform. Organic layer was separated and solvent was removed under vacuum. The monomer was then crystallized with chloroform and ethanol. (3.2 g, Yield: 95%) ¹H NMR (200 MHz, CDCl₃) δ 6.87 (t, *J* = 3.3 Hz, 1H), 6.58 (d, *J* = 3.7 Hz, 1H), 4.60 (s, 2H), 3.48 – 3.30 (m, 4H), 2.93 (t, *J* = 6.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 143.90, 130.22, 126.32, 110.25, 77.80, 77.48, 77.16, 77.16, 41.91, 31.54, 31.39.

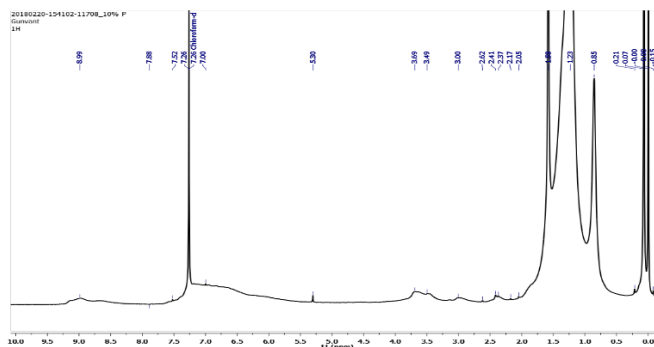
¹H-NMR of Br-Th-Urea:**Synthesis of 6,6'-dibromo-N,N'-(2-octyldodecyl)-isoindigo**

To a suspension of 6,6'-dibromoisoindigo (3 g, 7.14 mmol) and potassium carbonate (2.95 g, 21.42 mmol) in dimethylformaldehyde (DMF) (60 mL), 1-bromo-2-octyldodecane (6.42 g, 17.85 mmol) was injected through a septum under nitrogen. The mixture was stirred for 12 h at 90 °C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with (CH₂Cl₂: Hexane = 1:1) to give 6,6'-dibromo-N,N'-(2-octyldodecyl)-isoindigo (5.5 g; 78.7 %) ¹H NMR (200 MHz,

CDCl₃) δ 9.06 (d, *J* = 8.6 Hz, 2H), 7.16 (dd, *J* = 8.6, 1.7 Hz, 2H), 6.89 (d, *J* = 1.7 Hz, 2H), 3.61 (d, *J* = 7.3 Hz, 4H), 1.88 (s, 2H), 1.24 (s, 82H), 0.87 (t, *J* = 6.2 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 168.29, 146.38, 132.75, 131.17, 126.82, 125.27, 120.55, 111.72, 77.48, 77.16, 77.16, 76.84, 44.85, 36.23, 32.06, 32.01, 31.64, 31.08, 30.12, 29.77, 29.74, 29.68, 29.49, 29.43, 26.50, 22.84, 22.81, 14.25.

¹H-NMR of Monomer 1:**Synthesis of P10 Polymer**

Tin-monomer (0.1014 mmol, 50 mg), Monomer 1 (0.0912 mmol, 99.5 mg), Monomer 2 (0.00942 mmol, 4.41 mg), Pd₂(dba)₃ (5 mg) and P(*o*-tol)₃ (8 mg) were added in Schlenk tube. Tube was degassed with high vacuum and filled with argon gas. Chlorobenzene (6 mL) was added to a Schlenk tube. The mixture was stirred at 110 °C. The mixture was stirred for about 48 hours. Then the mixture was cooled down to room temperature, and poured into methanol and stirred for 2 h. The precipitate was collected by filtration. The product was purified through Soxhlet extraction using methanol, hexane and acetone to remove oligomers. The remaining polymer was extracted with hot chloroform in an extractor for 12 h. After removing the solvent, a dark blue solid was collected.

¹H-NMR of P10 Polymer**RESULTS AND DISCUSSION**

The different derivatives of urea group have been used particularly in paints, polymers and starting material in various agrochemical industries. The conventional synthetic strategies include reaction of amine with Phosgene and Tri-phosgene. Considering the poisonous nature of phosgene its safer

derivatives like carbonates,²⁴ N,N-carbonyldiimidazole,²⁵ 1,1-carbonylbisbenzotriazole,²⁶ S,S-dimethylthiocarbonate,²⁷ S-methylthiocarbamate,²⁸ formamides,²⁹ chloroformates, and others³⁰ have also been employed. However, these derivatives required more than one step to get final product and required conventional purification techniques. We started the synthesis of Br-Th-Urea Monomer (**2**) by reacting it with triphosgene. In first step, we reacted the 2-Thiopheneethylamine with triphosgene. Instead of going tedious and lengthy purification method, we separate Th-Urea (**1**) by precipitating it with ethyl acetate. After several wash, we were able to get white crystalline powder in 98% yield. Br-Th-Urea Monomer (**2**) was obtained by reacting Th-Urea (**1**) with N-Bromo succinimide. The reaction was completed within an hour and the product was then purified by crystallisation using CHCl₃:Ethanol (8:2) mixture. The ¹H-NMR, ¹³C-NMR spectroscopy and mass spectrometry suggest the presence of single molecule in the pure form. Further, we grow single crystal of Br-Th-Urea Monomer (**2**) and studied its crystal structure (Figure 2a). It was observed that the urea group shows intermolecular h-bonding between two monomers. The results were confirmed by concentration dependent ¹H-NMR experiment. Further, we were interested to check its applicability as CBS in the D-A conjugated polymers. For this purpose, we choose *i*-Indigo and 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene

for the synthesis of random block copolymer with 10 % molar ratio of Br- Th-Urea Monomer (**2**). The polymer was synthesized using stille type polycondensation reaction. The structure of monomer and polymer is shown in Figure 1 and Scheme 1.

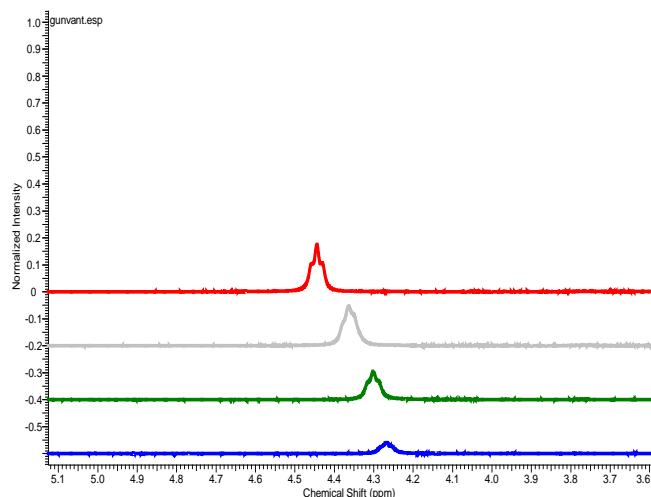
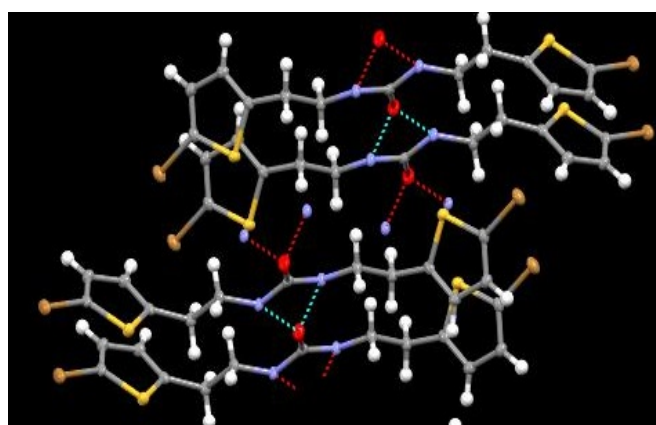
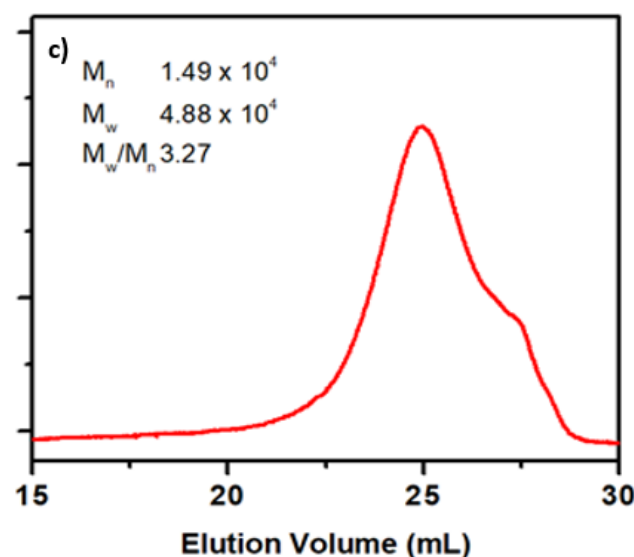
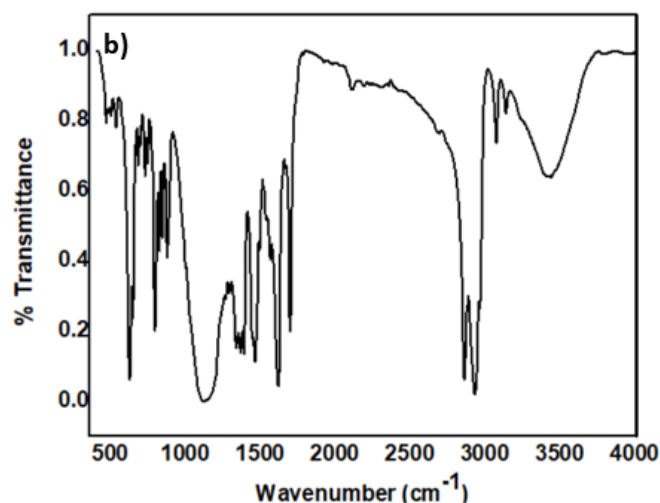
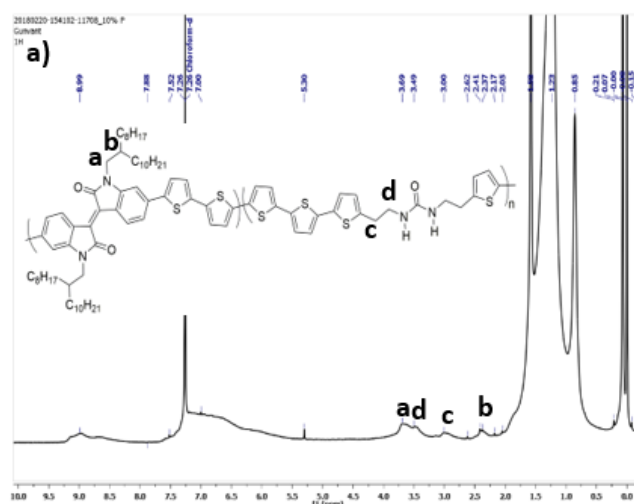


Figure 2: Crystal structure and Packing of Br-Th-Urea (a) and Concentration dependent ¹H-NMR zoomed (b) Solvent:CDCl₃



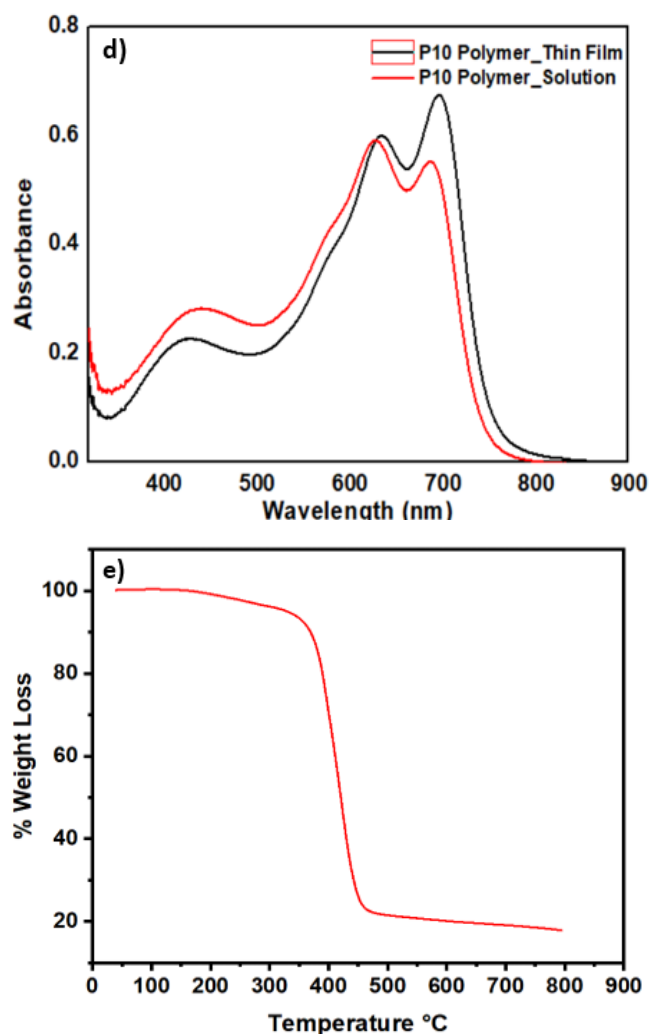


Figure 3: Characterization of P10 Polymer; $^1\text{H-NMR}$ Spectra, Solvent: CDCl_3 (a), Solid state IR Spectra recorded using Na-pellet (b), GPC graph (c), UV-Vis Spectra, Solvent: CHCl_3 (d) and TGA Graph (e).

The polymer was characterized by $^1\text{H-NMR}$, Infrared spectroscopy, Gel permeation Chromatography (GPC), UV-Vis spectroscopy and Thermogravimetric analysis (TGA). $^1\text{H-NMR}$ spectra of polymer show peaks at δ 3.00 ppm corresponds for ($-\text{CH}_2$) group attached to thiophene ring denoted as 'c' and another peak δ 3.49 ppm corresponds for another ($-\text{CH}_2$) attached to urea group denoted as 'd'. This indicated the presence of Monomer (2) in the polymeric backbone (Figure 3 a). Further IR Spectroscopy shows the peak at 3140 cm^{-1} corresponds for the N-H stretching frequency and broad peak in the $3400\text{--}3600\text{ cm}^{-1}$ related to the H-bonding stretching region. From this we can say that Br-Th-Urea Monomer (2) has been successfully incorporated into the polymeric backbone. The molecular weight of the polymer was calculated using GPC (Figure 3 c). Polymer shows PDI of 3.27 with the molecular weight in acceptable range. Thermal analysis suggest that the polymer is stable at higher temperature and shows 5% degradation at $350\text{ }^\circ\text{C}$ (Figure 3 e). The thermal stability ensures the processing of such polymer in

electronic device at higher temperature. The success of D-A conjugated polymer in electronic device lies in its electronic properties, electronic properties is crucial for the calculation of band gap³¹. The P10 Polymer exhibit absorption properties typical for many D-A conjugated polymers wherein higher energy band ($400\text{--}500\text{ nm}$) corresponded for $\pi\text{-}\pi^*$ transition and lower energy band ($525\text{--}775\text{ nm}$) related to donor to acceptor charge transfer (Figure 3 d). We recorded solution state (in CHCl_3) as well as thin film prepared by spin coating chloroform solution of polymer on glass substrate. Though polymer show similar spectra both in solution as well as in solid state, there is distinct red shift of 10 nm observed in thin film state. This red shift indicated that the h-bonding has certain effect on the morphology of the polymeric chain in solid state. However, the study of the effect of the h-bonding on the solid-state properties of the polymer is not the interest of our current manuscript, we limit ourself to the understanding the basic properties of h-bond containing urea monomer as CBS in the polymeric backbone.

CONCLUSION

We were successfully able to synthesise and purify urea based "CBS" linker without going into a tedious process of work-up and purification. We successfully able to study the crystal structure of Br-Th-Urea monomer and incorporated this monomer into *i*-indigo based D-A conjugated polymer. The polymer shows properties in corroboration with typical D-A conjugated polymer thus makes the polymer a potential candidate to be used in electronic device applications. This simple purification approach can extend to various h-bonded systems with flexible linkers.

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CONFLICT OF INTEREST

Authors declare no conflict of interest.

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