

A Review on Synthetic Approaches for Preparation of Donor-Acceptor Conjugated System.

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A Review on Synthetic Approaches for Preparation of Donor-Acceptor Conjugated System

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Abstract

The importance of donor-acceptor conjugated molecules has been increased since last few decades. These molecules are attracting great attention in the field of academics and also in industries. These molecules contain conjugated system with electron donor (rich) and electron acceptor (deficient) group attached to it. In these molecules, the electrons are transferred from HOMO of electron donating unit to LUMO of electron accepting unit. These conjugated molecules have wide applications in solar cells, bio sensors, photovoltaics, organic field transistors and many others. Many researches have been done on these conjugated molecules so as to encourage these materials as a potential candidate for optoelectronic and electroluminescent properties. This review gives an outline of the synthesis of various donor acceptor conjugated molecules by alternatively combining different acceptor units and donor units using different cross coupling reactions like Stille coupling reaction, Buchwald-Hartwig coupling, Suzuki coupling, direct arylation, Ullman cross coupling and Eglinton-Glaser coupling reactions.

Keywords: donor acceptor, conjugated system, monomer, coupling reaction

Introduction

Natural photosynthetic reactions give us the blueprints for sunlight harvesting, hence give a chief reason for studying electron donor-acceptor systems studies and characterizing them (Kaur et al., 2020). Organic molecules which has both an electron acceptor on one end and an electron donor group on other end of conjugated pi electron system have a significant importance in the field of materials chemistry (Zajac et al., 2008) because of diversity in their high charge mobility (Kang et al., 2019), chemical structure, solution processability, flexibility and stretchability which in turn make these molecules perfect for manufacturing of electronic devices which have low cost and large area (K. Huang et al., 2020). The conjugated system provides the rigidity to the donor acceptor conjugated molecules, as a whole it is considered as a backbone of molecule (Albinsson et al., 2007). Conjugated polymers are very vital molecules for researchers in the field of both academics as well as industries (C. Liu et al., 2015). These polymers show interactions in atomic orbital which results in absorbing a wide range of sunlight (Mahesh et al., 2019). Different methods have been tried to prepare

low band gap conjugated polymers like steric hindrance, by increasing chain length effectively, and designing of molecules having donor-acceptor system, among all of them, donor acceptor method is a nice method for preparing high performance conjugated polymers(Jian et al., 2018). The donor acceptor conjugated molecules, also known as push pull system with specified energy levels and energy gaps(Rahmanudin et al., 2019), are synthesized when the electrons are transferred from electron rich molecules HOMO to the electron deficient molecules LUMO(Y. Liu et al., 2018). When different conjugated systems were synthesized when electron deficient group was made to react with electron rich group, resultant conjugated system has better properties for reduction of band gap (E_g). If we modify the molecular structures of conjugated system, properties like band gap, stability (chemically or thermally), solubility and electrochromic characteristics are boosted(Cansu-Ergun, 2018). The best way for synthesis of these type of molecules is to firstly synthesize donor and acceptor monomer independently, after that polymerizing via cross coupling reaction using transition metal catalyst(Wu et al., 2015). They have unique properties like spintronics(London et al., 2019), electrical conductivity, non-linear optical (NLO) properties(Ohtani et al., 2019) electroluminescence(Meier, 2005) and biological applications(Sinkeldam et al., 2010). The donor-acceptor conjugated polymers have alternative electron deficient and electron rich units that are attractive because of optoelectronic properties(X. Wang & Wang, 2014) and this can be used as a powerful approach towards redox and photophysical characteristics of linear donor acceptor π -conjugated polymers in material chemistry(Izumi et al., 2020). If the donor-acceptor are strong, then they shows high conductivity than those having weak donor-acceptor system(Cai et al., 2018).

The donor acceptor conjugated polymers are integral part of light emitting diodes (LED)(Y. Li et al., 2020), photovoltaics cells, transistors(Ku et al., 2012), solar cells, television, mobile phone screens, biosensor(Cansu-Ergun, 2018), bioimaging(Izumi et al., 2020), memory devices(Z. Wang et al., 2018) and absorption materials(Gu et al., 2017). Also, they are gaining interest in electrochromic applications like reflectance mirrors, smart window and military camouflage and displays because of their excellent processability, fast switching rate(Yan et al., 2020), superior coloration efficiency, long term stability and high optical contrast ratios(Jian et al., 2018). These molecules also have application in designing photocatalysts for photocatalytic hydrogen production(L. Li et al., 2016), photoreduction of CO_2 to fuels containing hydrocarbon(Song et al., 2020), semiconductors(Van Mullekom et al., 2001), carbon nanotubes(de Araujo et al., 2020), fluorescent dyes (Jaswal& Kumar, 2019), neutral radical species(L. Huang et al., 2020), photocatalysis(Guo et al., 2020), and also show pharmacological properties(Ou et al., 2019). These molecules can be perfect candidate for drug delivery in cancer treatment(Z. Wang et al., 2019)and are helpful water splitting(Hayat et al., 2020) and in energy conservation because of its abundance in nature and nontoxic nature(Joo et al., 2018). These molecules show the phenomenon of phosphorescence at room temperature and fluorescence i.e. thermally activated(D. Zhang & Heeney, 2020). For practical applications of donor acceptor conjugated polymers, many effective methods have been developed, in which some important concerns are taken care of ,

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such as economic and environment friendly by reducing the number of steps in the synthesis(Kuwabara&Kanbara, 2020).

So, there are various different methods for the synthesis of various donor acceptor conjugated molecules such as Stille coupling reaction(Jin& Lee, 2010), Buchwald-Hartwig coupling(Liao et al., 2018), Suzuki coupling(Filatov et al., 2010), direct arylation(Arylation, 2011), Ullman cross coupling(Desymmetrization et al., 2016) and Eglinton-Glaser coupling reactions(Online, 2014).

2. Materials and Methods

2.1. Synthesis of conjugated donor-acceptor polymers comprising Difluorothienylethylene-bridged Methyleneazaioxindole (FVTAI) and Methyleneoxindole (FVTI) as acceptor units.

From the two novel difluorothienylethylene-bridged methyleneazaoxiindole (FVTAI) and methyleneoxindole(FVTI) used as acceptors units and six FVTAI AND FVTI based donor acceptor copolymers were developed. Based on the optimized backbone conformations of conjugated system, it was revealed that there were intra molecular noncovalent interactions in the conjugated polymers.

The pathway for the synthesis of FVTI and FVTAI which is based on 8 and 4 monomers and donor acceptor copolymers P1-P3F are given in the Figure 1. High yields of 6-bromo-1-(2-decyltetradecyl)indolin-2-one, 2, was obtained by reducing, 6-Bromo-1-(2-decyltetradecyl)indoline-2,3-dione,1, with hydrazine hydrate. The purple colour solid of FVTI based monomer,4 was having moderate yield. It was obtained by performing Knoevenagel condensation reaction under weak basic conditions, between 2 and (E)-5,5'-(ethene-1,2-diyl) bis(4-fluorothiophene-2-carbaldehyde), 3. 6-Bromo-1-(2-decyltetradecyl)-1H-pyrrolo[2,3-b]-pyridine, 5, when treated with pyridinium hydrobromide perbromide, gives the intermediate molecule,6.

This intermediate,6 is converted to 7 with 92% yield, when countered with Zn powder in THF in the existence of NH₄Cl. Similarly, the Knoevenagel condensation reaction was performed between 7 and 3, which resulted into FVTAI based monomer, 8, which is solid of dark purple colour. Stille copolymerization reaction was performed for monomers 4 and 8 separately with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 9a, (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl) bis(trimethylstannane), 9b, (E)-1,2-bis(5-(trimethylstannyl) thiophen-2-yl) ethene, 10a, or (E)-1,2-bis(3-fluoro-5-(trimethylstannyl) thiophen-2-yl) ethene, 10b, to give the resulted crude polymers P1-P3F respectively. Purification was done by the method of Soxhlet extraction by using solvents like methanol for 9a, acetone for 9b, n-hexane for 10a and o-dichlorobenzene for 10b. NMR spectra confirmed their chemical structures and high temperature gel permeation chromatography evaluated the elemental analysis.(Y. Zhou et al., 2018)

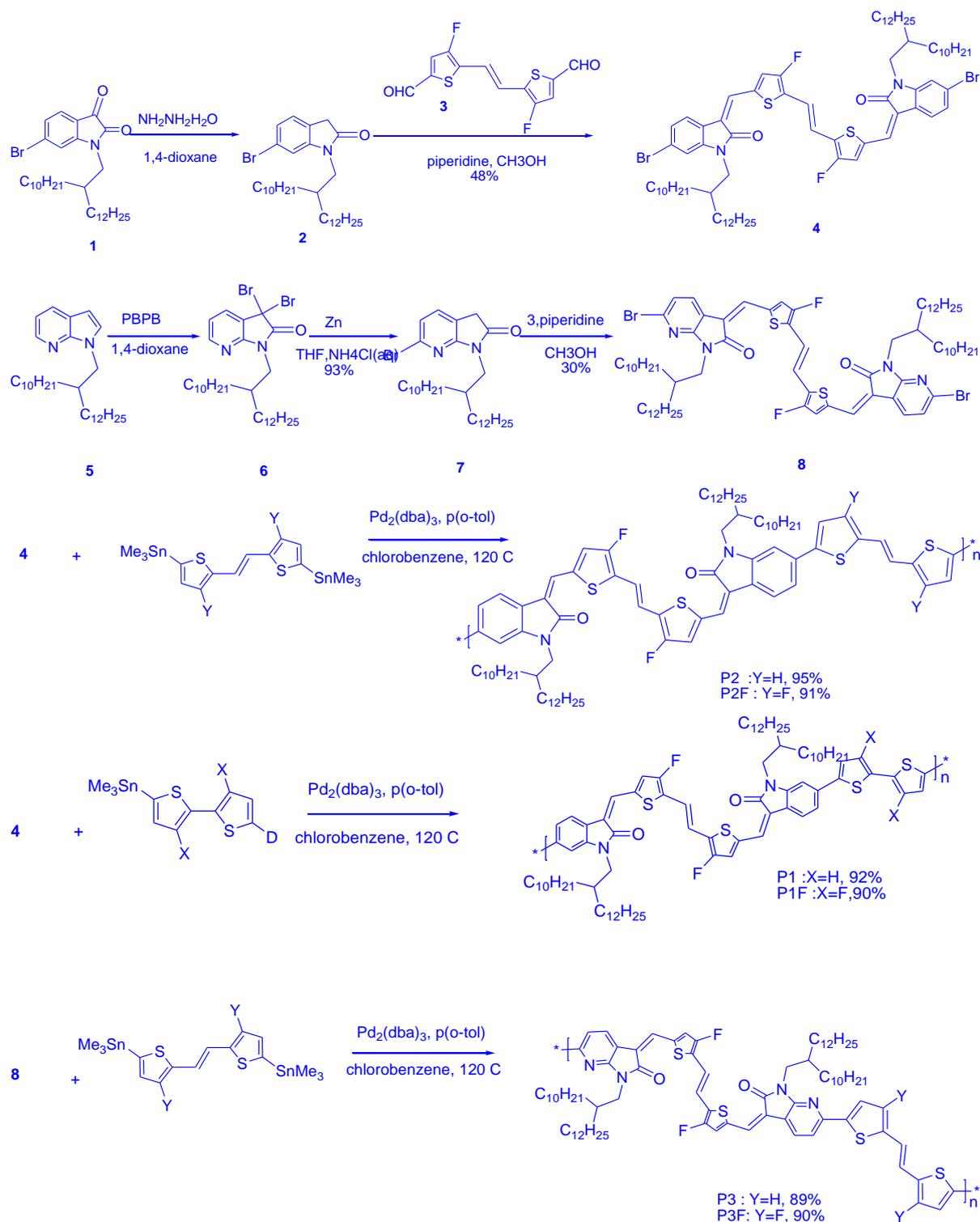


Figure 1: Synthetic route of 4 and 8 monomers and donor-acceptor conjugated Copolymers P1–P3F. (Y. Zhou et al., 2018)

2.2. Synthesis of Donor–Acceptor conjugated system i.e., 1,2,4,5-Tetrazines

1,2,4,5-tetrazines synthesis is recognized for enhancing fascinated substantial interest after start of bioconjugation. For the past many decades, 1,2,4,5-tetrazine molecules have their application in the various fields like coordination chemistry, energetic materials, synthesis of

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natural products, and organic electronics. 1,2,4,5-tetrazines synthesis was done by applying Buchwald-Hartwig coupling reaction and efficaciously produced a number of new donor acceptor 1,2,4,5-tetrazine molecules which are having good yield from 61-72%.

3-(4-bromophenyl)-1,2,4,5-tetrazine, **1**, is the substrate of tetrazine as they are used as bio-orthogonal click. The metal free synthetic approach was used for the preparation of tetrazine **1**. Strong electron donor groups like phenoxazine, 9,10-dihydro-9,9-dimethylacridine, phenothiazine and carbazole. These molecules having donor acceptor systems show immense importance in the field of organic electronics because of the excited states having charge transfer which is induced in the presence of electron donor acceptor system.

The selection of base, ligand and catalyst plays crucial part for good yields of the product. By using precursor **1** and phenothiazine, phenoxazine or 9,10-dihydro-dimethylacridine as a donating (rich) group, three new donor acceptor-acceptor 3- monosubstituted tetrazines TA2-TA4 (unsymmetrical) was prepared and are having good yields ranging from 61-72%. Whereas bifunctional tetrazine precursor **2** by Buchwald-Hartwig coupling reaction prepared three donor- acceptor 3,6 disubstituted tetrazines TA5-TA7 (symmetrical) and lead to low yield but precursor was recovered in the large amount. So, it was concluded that tetrazine was more reactive than precursor **2**. So, by Buchwald- Hartwig cross coupling reaction total seven new tetrazines were prepared (Qu et al., 2020).

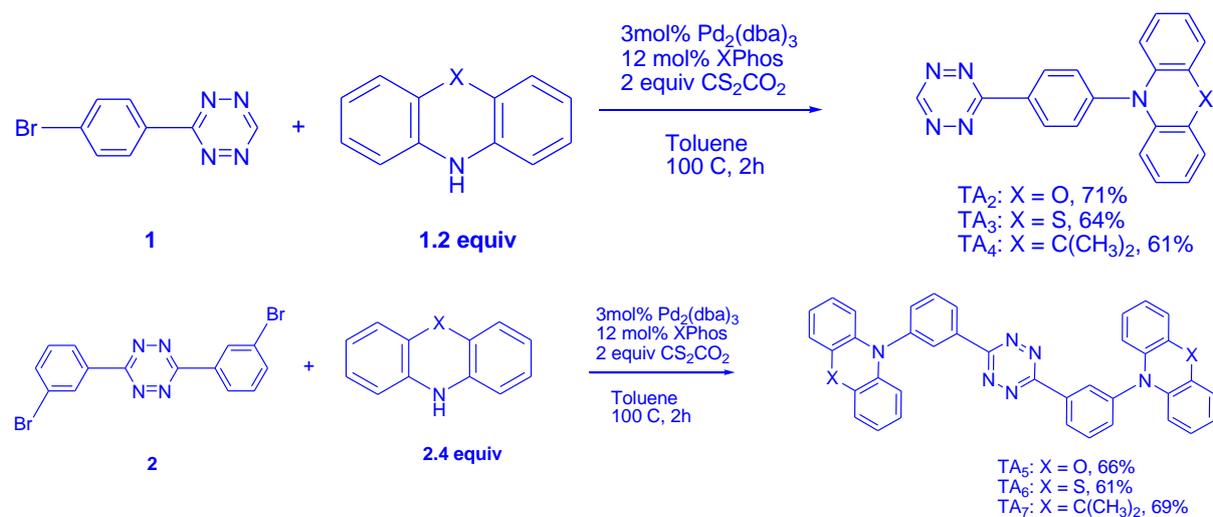


Figure 2: Synthetic route to 3-Monosubstituted Tetrazines (TA2–TA4, Unsymmetrical) and 3,6-Disubstituted Tetrazines (TA5–TA7, Symmetrical) (Qu et al., 2020).

2.3. Synthesis of donor acceptor conjugated molecules having Indanone-Condensed Thiadiazolo[3,4- g]quinoxaline as Acceptors.

Synthesis of two new indanone-condensed thiadiazolo[3,4-g]quinoxaline as acceptor groups that show LUMO levels and high electron affinities because of adding cyano or carbonyl group into the thiadiazolo[3,4-g]quinoxaline core. Also, synthesis of two molecules of conjugated polymers having donor acceptor system, having low band gap when the newly synthesized by thiadiazolo[3,4-g]quinoxaline (acceptor units) react with 2,5-bis(3-(2-decyltetradecyl)thiophen-2-yl)thieno- [3,2-b]thiophene (donor units) by Stille condensation.

The two polymers formed were having yield 90 and 93%. The structures of the product molecules were validated by using ^{13}C , ^1H NMR spectra and single crystals. Purification is done by Soxhlet extraction and precipitation. Also, the whole procedure is carried out in nitrogen atmosphere (Chen et al., 2019).

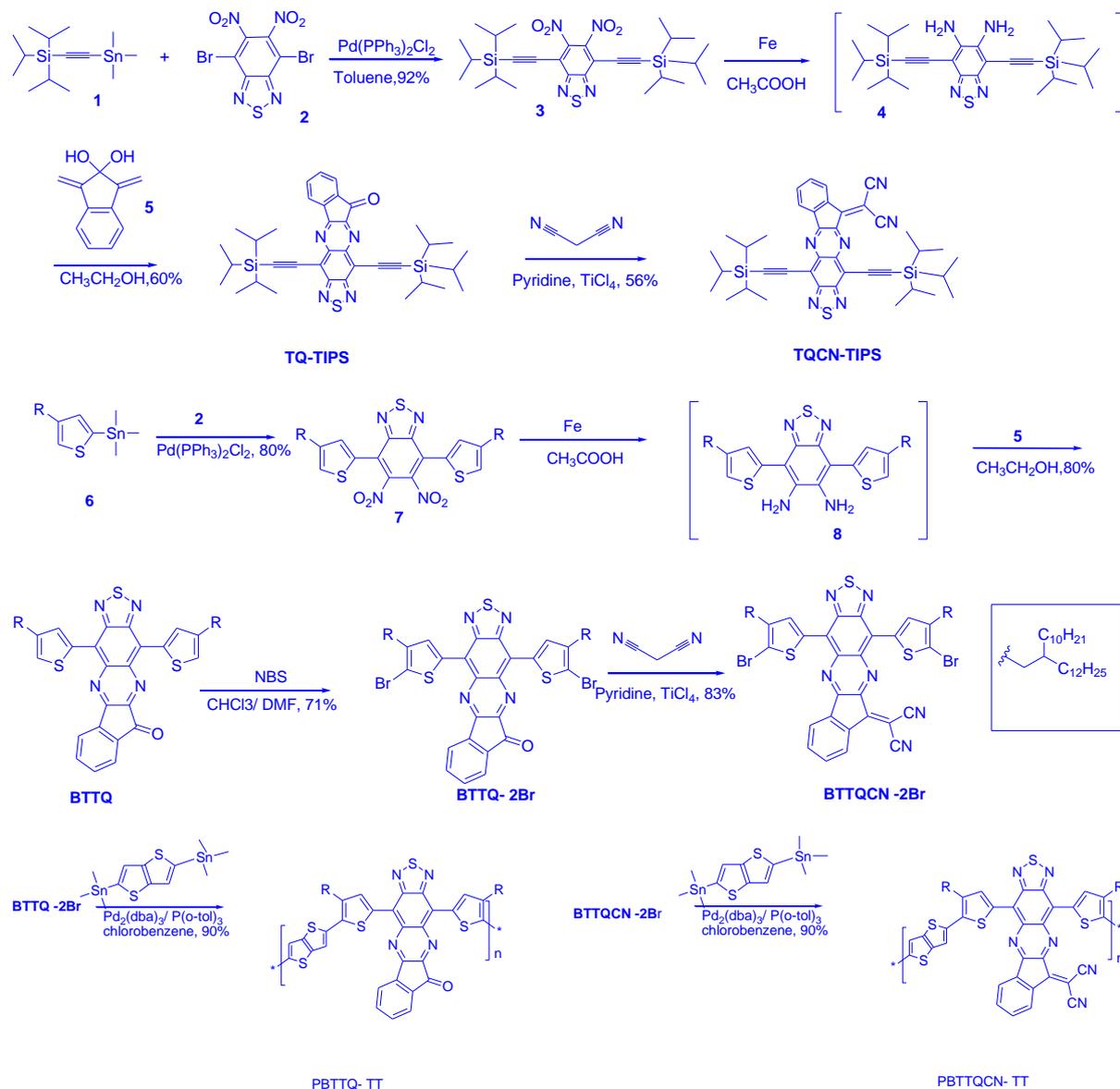


Figure 3: Synthetic routes to the thiadiazolo[3,4-g]quinoxaline as acceptors based model molecules. (Chen et al., 2019)

(TQ-TIPS: thiadiazolo[3,4-g]- quinoxaline, TQCN-TIPS: , BTTQ : benzo[1,2-c:4,5-c']-bis[1,2,5]thiadiazole quinoxaline ,BTTQ-2Br : thieno[3,4-c][1,2,5]thiadiazole)

2.4. Synthesis of n type poly(peryene diimide-altoligothiophene) copolymers comprising of donor acceptor system.

Perylene diimide polymers gained importance as a new type of polymers i.e., n-type that have great application in polymers solar cells. These perylene diimide molecules being an electron deficient can easily copolymerised with electron rich unit so as to show optoelectronic

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properties (E. Zhou et al., 2011). Donor-Acceptor conjugated polymers with n-type properties are prepared by linking an acceptor unit with donor monomers which are responsible for controlling HOMO and LUMO levels so that they can tune the gaps in the energy band. Donor-acceptor molecules of perylene diimide were synthesized by substituting perylene base in bay position which also contains oligothiophene and with dithienothiophene group, a polymer was prepared. Two novel copolymers with alternative donor-acceptor groups, P1 and P2, were synthesized which contain a perylene diimide unit in the main chain linked to bay position with terthiophene and bithiophene units. By Stille reaction between 5,50-bis-(trimethylstannyl)-2,20-bithiophene or 5,500-bis-(trimethylstannyl)-2,20:50,200-terthiophene and N,N-bis(10-nonadecyl)-1,7-dibromo-3,4,9,10-perylene diimide, two copolymers were synthesized. Both copolymers have high solubility and are easily processable in THF, chloroform and chlorobenzene (Kozma et al., 2010).

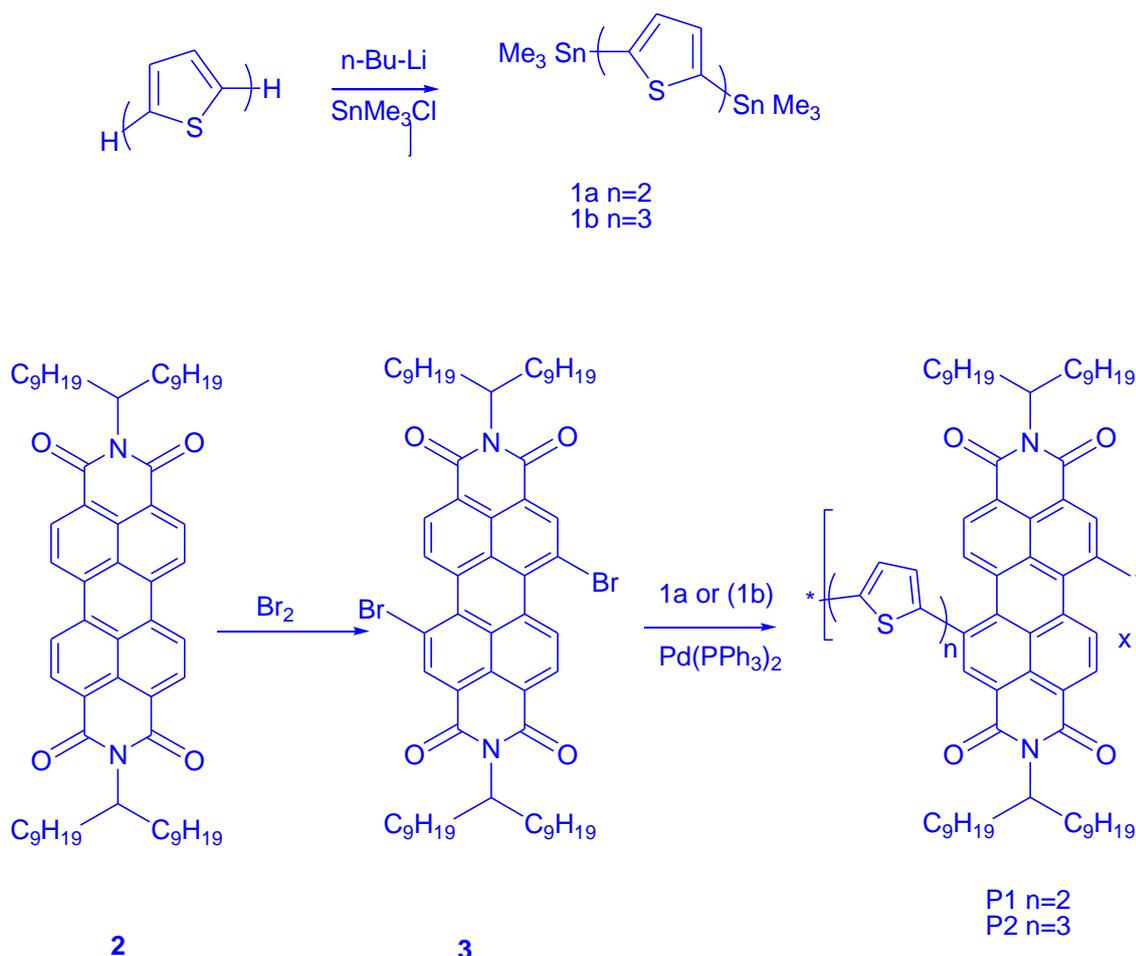
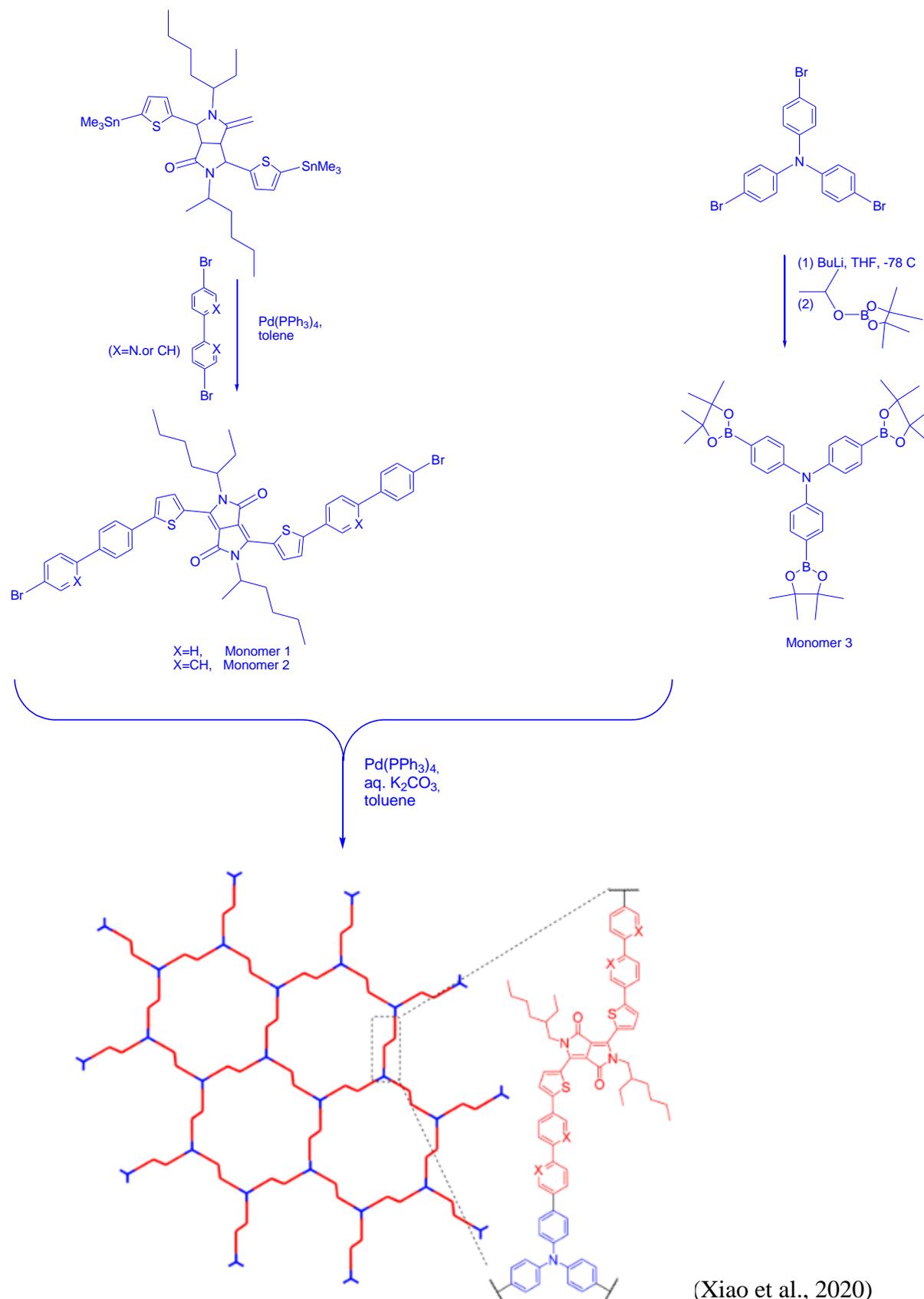


Figure 4: Synthetic route for polymers poly(perylenediimide-altoligothiophene) (Kozma et al., 2010)

2.5. Synthesis of Diketopyrrolopyrrole Conjugated Microporous Polymers consisting of donor-acceptor system.

Conjugated microporous molecules are prepared when diketopyrrolopyrrole (DPP) combine with biphenyl (bph), bipyridyl (bdy) and triphenylamine (TPA) units. The two synthesized polymers i.e., DPP-bph-TPA and DPP-bpy-TPA have similar structures. The two conjugated microporous polymers synthesized, DPP-bph-TPA and DPP-bdy-TPA, have TPP which is a

strong electron donor group, DPP which is a strong electron acceptor group biphenyl(bph) or bipyridyl(bdy) which are second electron donor or acceptor unit.



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Figure 5: Synthetic route of Diketopyrrolopyrrole Conjugated Microporous Polymers

The synthesis of DPA-bph-TPA and DPA-bdy-TPA is shown in Figure 5. Suzuki-coupling polymerisation takes place between DPP monomer(linear) having bromine at the end (monomer 1 or 2) and monomer TPA which has three borylated groups. The two conjugated microporous molecules have insolubility in common solvents. Their structures were confirmed by ^{13}C NMR, FTIR and elemental analysis(Xiao et al., 2020).

2.6. Synthesis of Donor Acceptor 2,1,3-benzothiadiazole and benzo[1,2-b:4,5-b']dithiophene based copolymers via direct-arylation.

The polymer named PBDTBT contains benzo[1,2-b:4,5-b']dithiophene (BDT) and 2,1,3-benzothiadiazole (BT) as electron donor(rich) group and acceptor(deficient) group correspondingly. Both BT and BDT are the important components for the formation of conjugated polymers consisting of donor acceptor system. In the BDT component, two 2-hexyldecyloxy groups are long and have branches introduced to treat the good melting of PBDTBT in various solvent species. Direct arylation provides high molecular weight of PBDTBT with good regularity in quantitatively yield. Figure 6 shows the synthesis of PBDTBT by direct arylation coupling reaction when polymer is catalysed by palladium that occurred between two monomers namely, 4,7-Dibromobenzothiadiazole (BrBT) and 4,8-Di(2-hexyldecyloxy)benzo[1,2-b:4,5-b']dithiophene (HDBDT)(X. Wang & Wang, 2014).

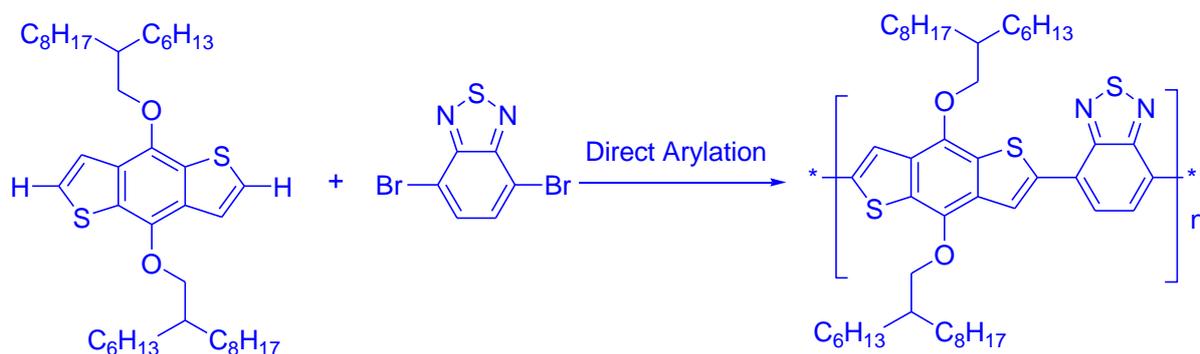


Figure 6: Synthetic Route to the PBDTBT(Polymer benzo[1,2-b:4,5-b']dithiophene 2,1,3-benzothiadiazole)(X. Wang & Wang, 2014)

2.7. Synthesis of Conjugated Macromolecules i.e., 3B2A and 4B2A consisting of donor acceptor system.

Electron donor (rich) and acceptor (deficient) molecules are the essential key components for synthesizing donor acceptor conjugated macromolecules. 4,7-bis(thienyl)-2,1,3-benzothiadiazole (BTTh2) act as an electron accepting unit and triphenyl ammine (TPA) as an electron donating group in the backbone of cyclic molecules. BTTh2 and TPA are linked to each other alternatively via acetylene as the acceptor and donor units correspondingly, and two macromolecules i.e., 3B2A and 4B2A were synthesized. They have different shapes, hexagonal for 4B2A and pentagonal for 3B2A.

The two cyclic conjugated macromolecules were synthesized by two different synthetic methods. 3B2A molecule was synthesized by a step wise and in a controllable manner as

depicted in Figure 7. By copper-palladium catalysed homocoupling reaction of monomer terminating with alkyne, M1 monomer, under copper-palladium catalysed Eglinton-Glaser coupling reaction conditions in dilute solution, the conjugated molecule, polymer, 3B2A is synthesized with an unsymmetrical structure having yield 21.4%. Whereas, 4B2A has a symmetrical structure and synthesized by fragment coupling method. When homocoupling reaction occurs between the two monomer fragments, M2 (C-shaped), there is intermolecular alkyne-alkyne interaction and 4B2A macromolecule is synthesized having yield 8.7% (S. Q. Zhang et al., 2017).

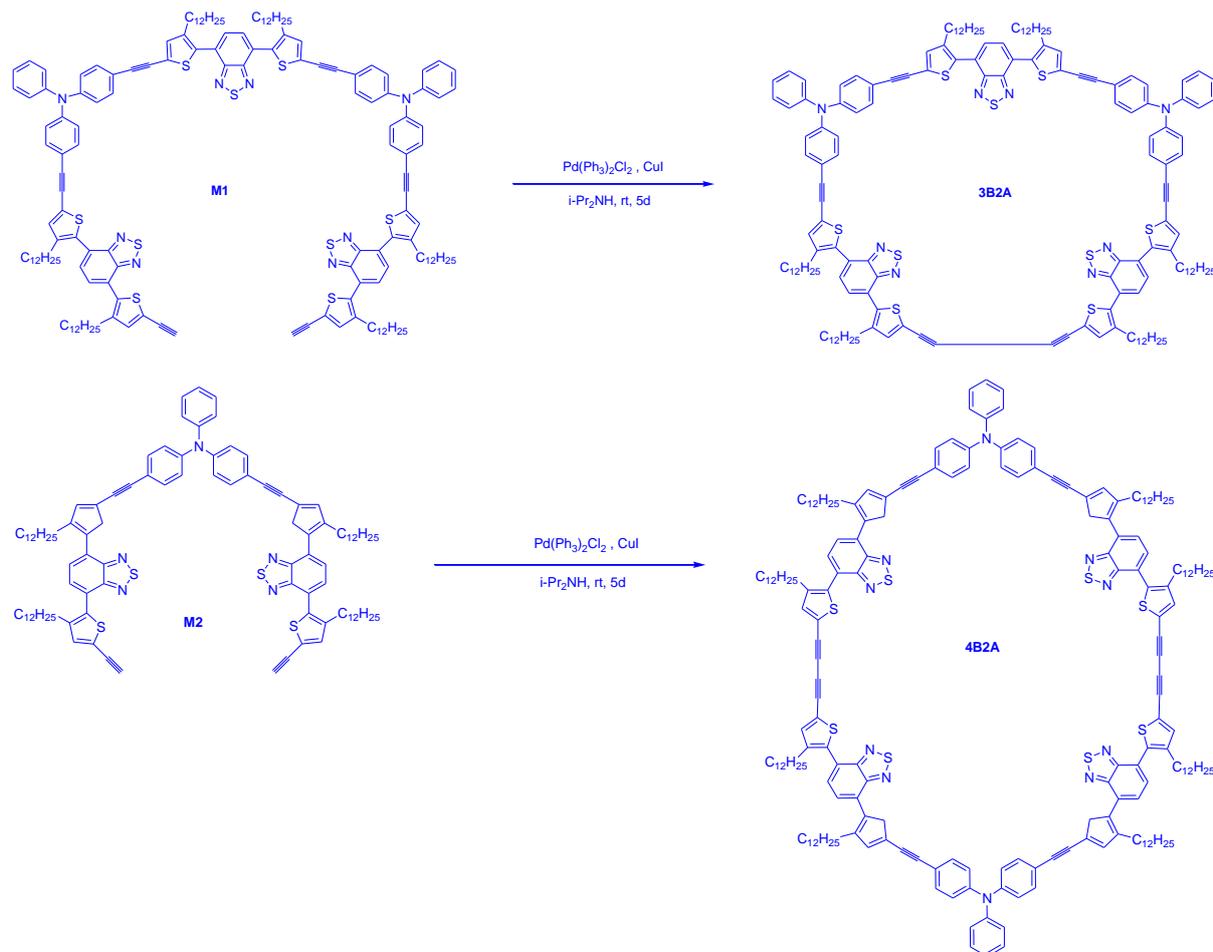


Figure 7: Synthetic route of cyclic conjugated macromolecules 3B2A and 4B2A. (S. Q. Zhang et al., 2017)

2.8. Synthesis of a series of conjugated system of covalent organic polymers, COP (monomers: 3, 8-Dibromo-phenanthroline (DBP) and 3, 6, 8-tetrabromopyrene (TBP)).

3, 8-Dibromo-phenanthroline (DBP) and 1, 3, 6, 8-tetrabromopyrene (TBP) and an electron acceptor (deficient) and donor (rich) respectively, act as building blocks for synthesizing the donor acceptor series of covalent organic polymers. These polymers are responsible for enhancing absorption of visible light and boosting the light induced carriers. To synthesize COP-TP_{x:y} where x and y are representing the fraction of TBP and DBP, two weak electron withdrawing group like benzene and pyrazine fused to get conjugated covalent organic polymers (COP). Among all the proportions of x and y, COP-TP_{3:1} shows excellent

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photovoltaic properties for different kinds of water quality like municipal water, simulated water, commercial water and deionised water. Figure 8 shows the synthesis of COP-TP_{x:y} by copolymerization which was done by Ullmann cross-coupling reaction of Yamamoto type using Nickel as catalyst (Y. Liu et al., 2018).

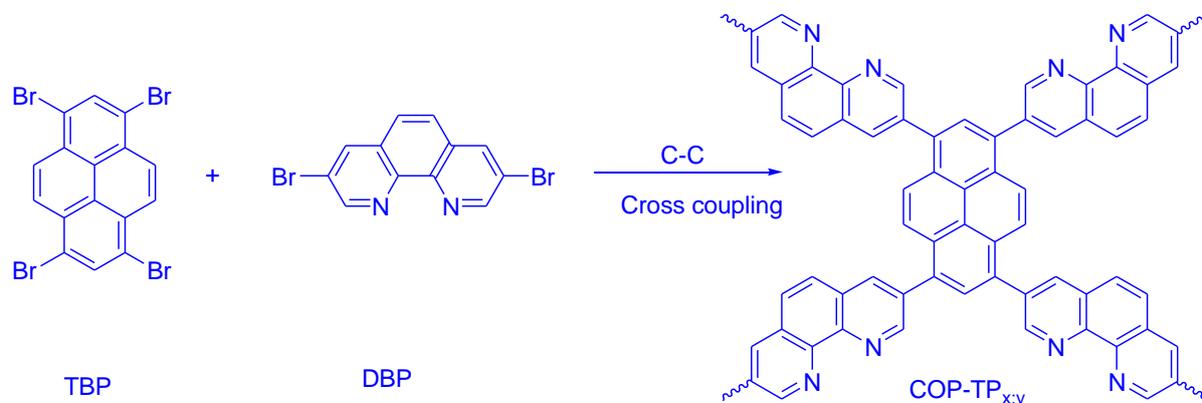


Figure 8: Route of synthesis of COP-TP_{x:y} by using monomers 3,6,8-tetrabromopyrene (TBP) and 3,8-Dibromo-phenanthroline (DBP) (Y. Liu et al., 2018)

3. Results and Discussion

We have discussed eight methods of synthesis of donor acceptor molecules which can have very applications in our life. Synthesis of conjugated polymers with donor acceptor system comprising Difluorothienylethylene-bridged Methyleneazaoindole (FVTAI) and Methyleneoxindole (FVTI) as acceptor units is done by performing Knoevenagel condensation reaction under weak basic conditions and Stille copolymerization reaction to result in various monomers 1-8 and polymers 1-3 having high yield. By applying Buchwald-Hartwig coupling reaction, 1,2,4,5-tetrazines were synthesized which results into many new donor acceptors 1,2,4,5-tetrazine molecules which are having yield up to 61-72%. Also, when thiadiazolo[3,4-g]quinoxaline react with 2,5-bis(3-(2-decyltetradecyl)thiophen-2-yl)thieno-[3,2-b]thiophene by Stille condensation, which results into two products i.e., donor-acceptor conjugated polymers with yield 90 and 93%. The two copolymers were also synthesized when 5,50-bis-(trimethylstannyl)-2,20-bithiophene or 5,500-bis-(trimethylstannyl)-2,20:50,200-terthiophene and N,N-bis(10-nonadecyl)-1,7-dibromo-3,4,9,10-perylene diimide react with each other via Stille reaction. Conjugated microporous molecules are prepared when diketopyrrolopyrrole (DPP) combine with biphenyl(bph), bipyridyl(bdy) and triphenylamine (TPA) units via Suzuki coupling polymerizing reaction. The polymer named PBDTBT contains benzo[1,2-b:4,5-b']dithiophene (BDT) and 2,1,3-benzothiadiazole (BT) as electron rich group and deficient group respectively by direct arylation. 4,7-bisthienyl-2,1,3-benzothiadiazole (BTTh2) act as an electron accepting unit(deficient) and triphenyl ammine (TPA) as an electron donating unit(rich) in the backbone of cyclic molecules. BTTh2 and TPA are linked to each other alternatively via acetylene as the acceptor and donor units correspondingly, and two macromolecules i.e., 3B2A and 4B2A were synthesized under copper-palladium catalysed Eglinton-Glaser coupling reaction conditions in dilute solution. Being an electron rich and deficient group 1,3,6,8-tetrabromopyrene(TBP) and 3,8-Dibromo-phenanthroline (DBP) respectively, act like

building blocks for synthesizing the donor acceptor series of covalent organic polymers via Ullmann cross-coupling reaction of Yamamoto type using Nickel as catalyst.

4. Conclusion

Here in this review, we discussed about synthesis of different donor-acceptor conjugated molecules that have important application part and are important in the past few decades. Different electron donating and electron withdrawing group plays key role for the synthesis of conjugated molecules. This review gives us the major idea about how different donor acceptor conjugated molecules were synthesized by different coupling reactions and giving different yields. This also gives an idea which coupling reaction gives us our desired conjugated molecules with good yield. Mainly used coupling reaction for the synthesis of conjugated molecules having donor acceptor system is Stille coupling reaction and also gives the high yield as compared to other coupling reactions.

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Conflicts of Interest

The authors declare that there is no conflict of interest.

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