

Oligothiophenes: Synthesis and Optoelectronic Properties

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Abstract

Oligothiophenes give a magnificent opportunity to explore its different synthesis and uses as in optoelectrical devices nowadays. In contrast, oligothiophenes afford higher purity and easy modification with several functional groups than their polymer counterparts. Recent work on functional oligothiophenes of advanced materials for organic electronic devices has been developed. In this study, the synthesis and characterisation of linear and fused oligothiophenes (e.g., oxidative coupling, palladium catalysed C-H homocoupling and cross-coupling) emphasises applications in various areas are addressed.

Keywords: OLED, oligothiophenes, organic photovoltaics, Rozen's reagent, Suzuki coupling.

Introduction

Oligothiophenes (Beaujuge and Fréchet, 2011), is the family of oligomers of thiophene. The organic materials show some advantage over inorganic material because of lightweight and good chemical tuning for the optoelectronic property. Thiophenes and oligothiophenes are not only represented in the synthesis of products (natural) and pharmaceuticals, but organic materials, especially thiophene-based molecules, have got great attention, mainly in making optoelectronic devices (Asoh et al., 2020). These molecules are stable under thermal and photochemical conditions and the crystalline property in them helps create holes in the compound that can conduct electricity. It also plays a role in the

conjugate π electron system by decreasing the HOMO-LUMO energy gap and making the molecules conduct electricity. Oligothiophenes and their functional derivatives are used in high technology operations such as organic photovoltaics (OPVs), organic semiconductor (OSC), organic field-effect transistors (OFET), organic light-emitting diode (OLED) etc. where the ability to functionalize the oligothiophenes backbone allows the fine-tuning of electronic properties. It gives an adorable platform to explore optical and electrical relationships between oligothiophenes. Oligothiophenes are highly pure that can be modified with functional groups to use it in a better way. Recently, some methodologies have been

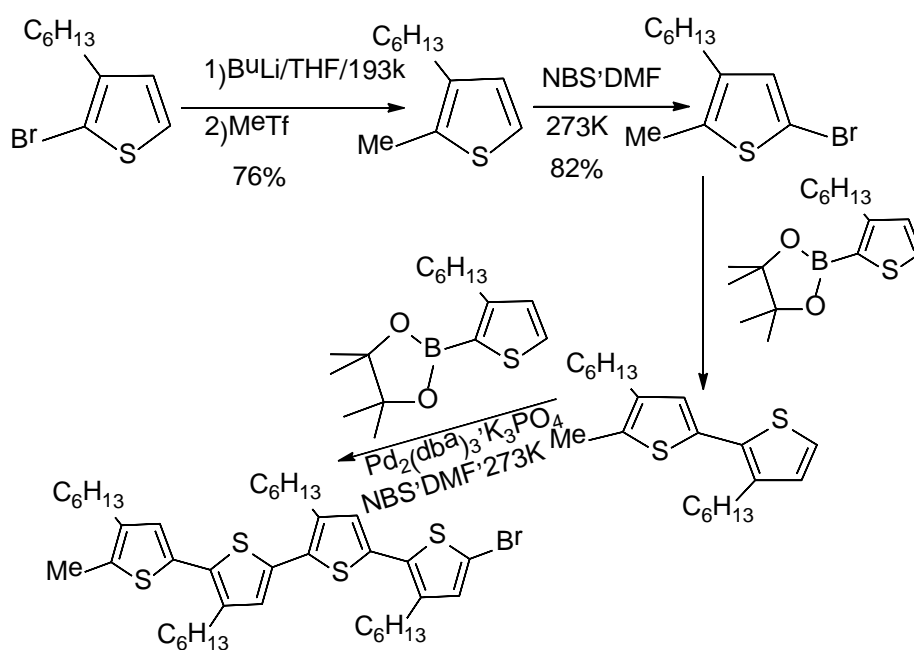
proposed for synthesizing oligothiophenes that can help humankind through their different properties. Moreover, the research works with oligothiophenes are very much cost-effective and eco-friendly and thus, it can make the path of researches wider.

In this article, the main focus is the synthesis and Opto-electrical properties of oligothiophenes. Furthermore, it allows differentiating between oligothieryl triphenylamines and their related linear oligothiophenes.

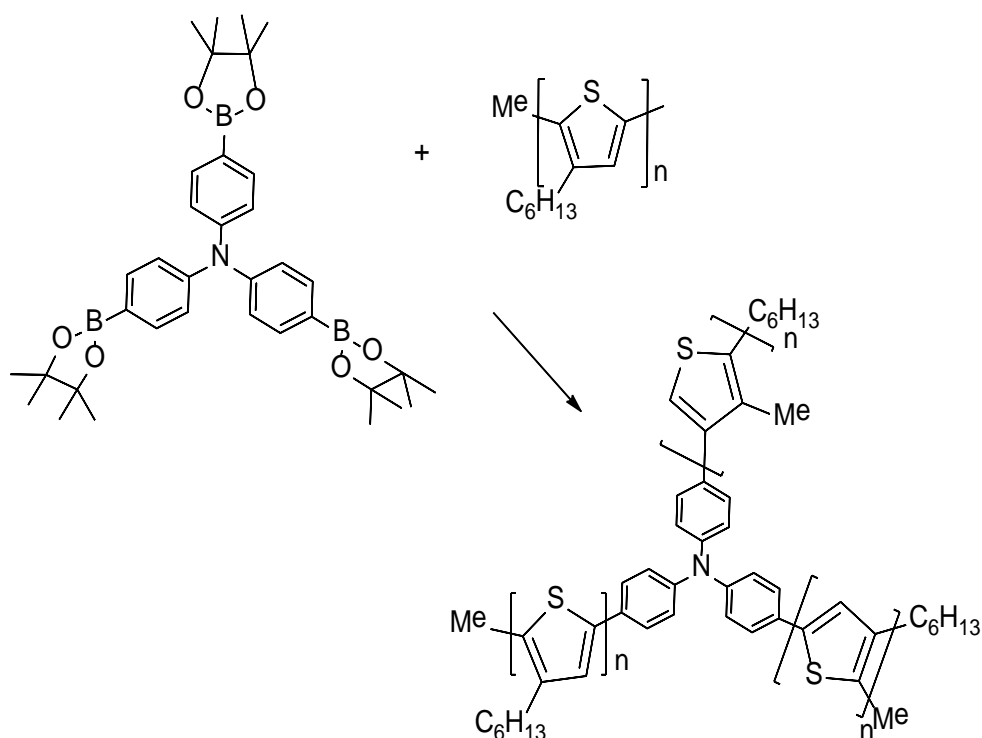
Formation of Oligothieryl triphenylamine

Cremer and his colleagues (Crème and Briehn, 2007) suggested several amorphous oligothieryl-triphenylamines covalently bonded to a core of triphenylamine (3-hexylthiophene). These systems vary in the length of the oligothiophene units (from

monothiophene to quaterthiophene) via palladium-catalyzed or platinum-catalyzed cross-coupled processes, which produces excellent results. These systems are different in size. The optical and electrochemical properties of these compounds were checked and compared to the corresponding parent linear non-functionalized oligothiophenes. It is proven that these newly synthesized hybrid holes (Bach et al., 2000) systems have perfect properties like absorption and emission. Moreover, these molecules exhibit fluorescence (Chen et al., 2007; Mitschke and Bäuerle, 2000) quantum yields which are high for thiophene based materials. The relationship between structure and property is established based on the providing data, providing a deeper insight into the difference between star-shaped (Thomas et al., 2002) structures and parent linear oligothiophenes.



Scheme 1. Synthesis of substituted terthiophenes.



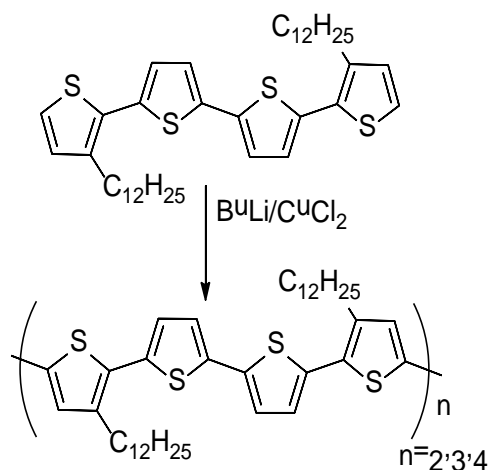
Scheme 2. Synthesis of Oligothiényl triphenylamine.

Oxidative Coupling of Thiophene Based Material

Due to the presence of oxidising agents such as FeCl₃, thiophene derivatives may be oxidised and subsequently dimerized by CuCl₂ to produce a mixture of s-conjugated (Zhang et al., 2014) oligomers. This technique has the benefit of allowing electron density to vary at various locations on the thiophene monomer; coupling occurs mainly at the positions with the highest electron density. As a result, this technique is extremely straightforward. Beaujuge and Fréchet (2011) found that it has a lot of coupling, which affects conjugation. However, a rise

in molecule conjugation produces a fast loss of reactivity, resulting in a short chain of oligomers.

The technique's drawback is the need to purify the ingredients (Takimiya et al., 2006). Because metal residues contaminate the intended products, repeated sublimation (Mishra and Bäuerle, 2012) and chromatographic separation (Tanaka et al., 2011) are required to purify the product. Bäuerle and colleagues recently published a paper on a novel 'metal template method to synthesis oligothiophenes'. The procedure is as follows:

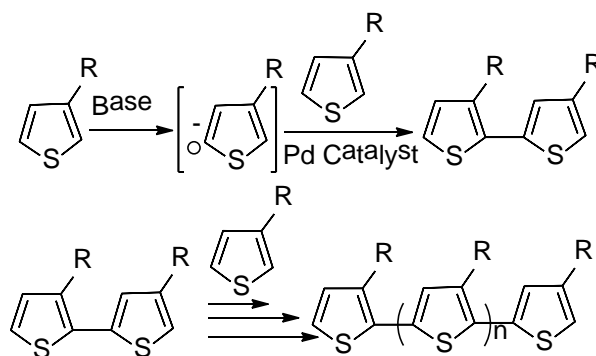


Scheme 3. Synthesis of oligothiophenes by oxidative coupling method.

Palladium-Catalyzed C–H Homo-coupling of Substituted Thiophene

Metal-catalyzed cross-coupling (Tan et al., 2009) has been invented for the synthesis of polythiophenes. These reactions occur by following the chain-growth mechanism. So it is challenging to synthesize oligomers with almost the same molecular weight. Scientists Mori and his companions developed a synthesis method involving the palladium-catalyzed (Brédas et al., 2002) C–H homocoupling (Rivnay et al., 2009) bromothiophene. This technique has oligothiophenes with C–Br bonds at

the terminal rings, which can be functionalized again. More recently, these scientists developed a procedure for the synthesis of oligothiophenes. Treatment of 3-alkylthiophene with Knochel–Hauser (Schuettfort et al., 2012) base ($TMPMgCl \cdot LiCl$) induces metalation (Gann et al., 2016) at the 5-position. Palladium is used as a catalyst here and form bithiophene. Then bithiophene molecule is firstly converted to the terthiophene and then quaterthiophene by the same mechanism.



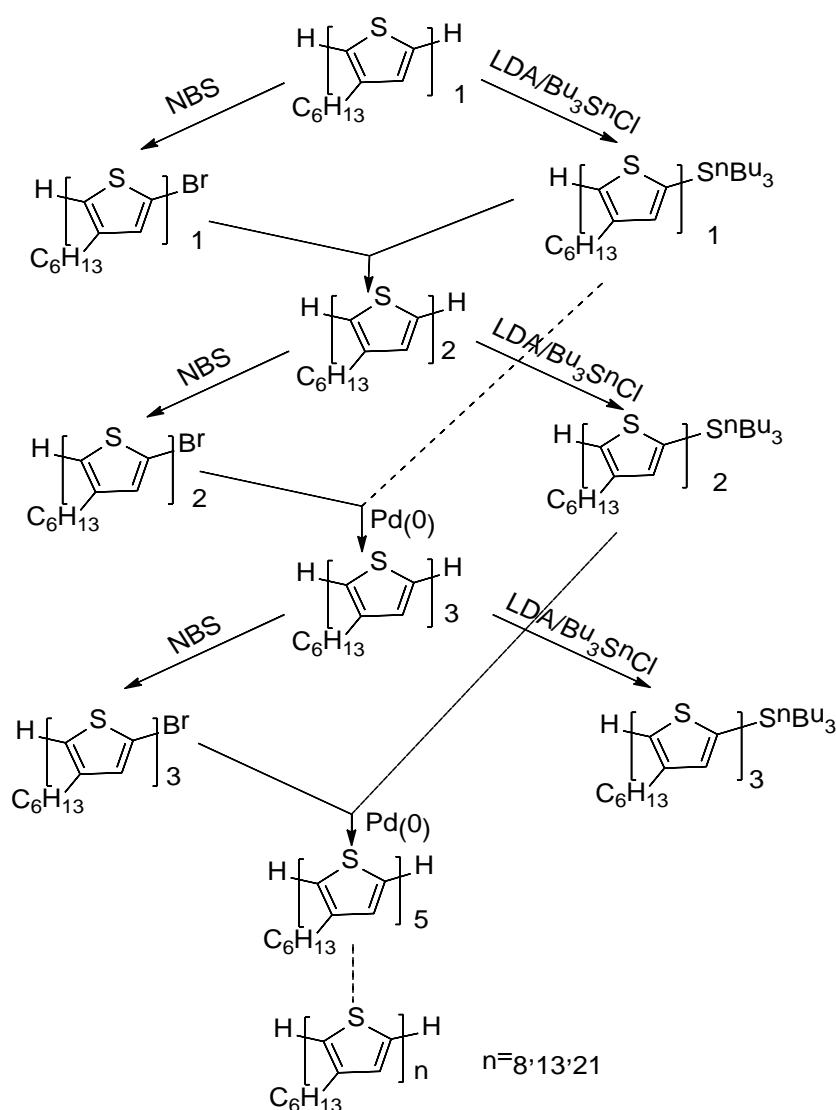
Scheme 4. Pd catalysed homocoupling reaction of 3-alkylthiophene in the presence of Knochel–Hauser base ($TMPMgCl \cdot LiCl$).

Palladium-Catalyzed Cross-Coupling of Substituted Thiophene

Long oligothiophenes are often made by adding bromine, tin(successively) to thiophene intermediates for palladium catalysed cross-coupling processes as Stille or Suzuki (Körzdörfer and Brédas, 2014). Using a Pd-catalyzed reaction, scientist Lei Zhang and his colleagues recently created a series of didodecyl quaterthiophene oligomers (McCullough, 1998) with up to 24 thiophene units (McCullough, 1998).

(Mannebach et al., 2013; Schulze et al., 2006). Due to the increased frequency of β -positions compared to α -positions, the reactivity at long oligothiophenes reduces while the probability of reaction at β -positions rises.

There is thus a significant problem, the separation of the α -products sought from the unwanted β products. Therefore, to prevent unwanted responses, the β locations must be blocked.

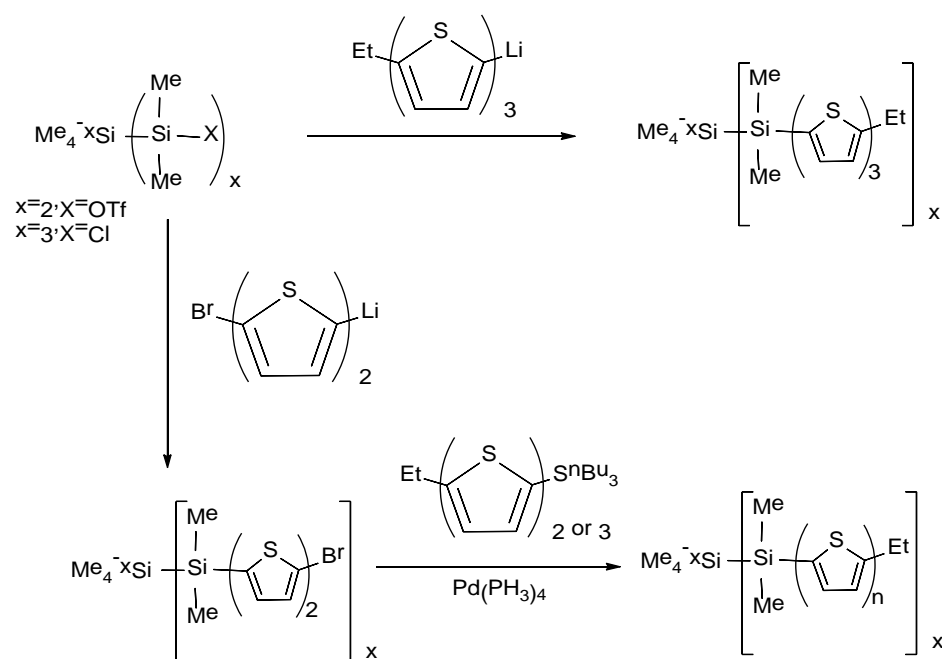


Scheme 5. Cross-Coupling reaction of substituted thiophenes catalysed by Pd.

Trisilanylene-Bridged Oligothiophenes

According to scientist Joji Ohshita (Ohshita et al., 2007) and his co-workers, films (spin-coated) of trisilanylene-bridged (Lee et al., 2009) oligothiophenes were used as semiconductors (p-type) in field-effect transistors (FET) (Rost et al., 2004). The most excellent FET performance was obtained by employing tris [(ethyl quinque-thiophenyl) dimethylsilyl] methylsilane as

the active material, which had an excellent field-effect mobility and on/off ratio (Murphy and Fre, 2007). Furthermore, the trisilanylene-bridged oligothiophenes were photoactive and irradiated (Murphy and Fre, 2007; Fujii et al., 2009; Niebel et al., 2012) films in the air reduced hole mobility, allowing them to be used as semiconducting materials.

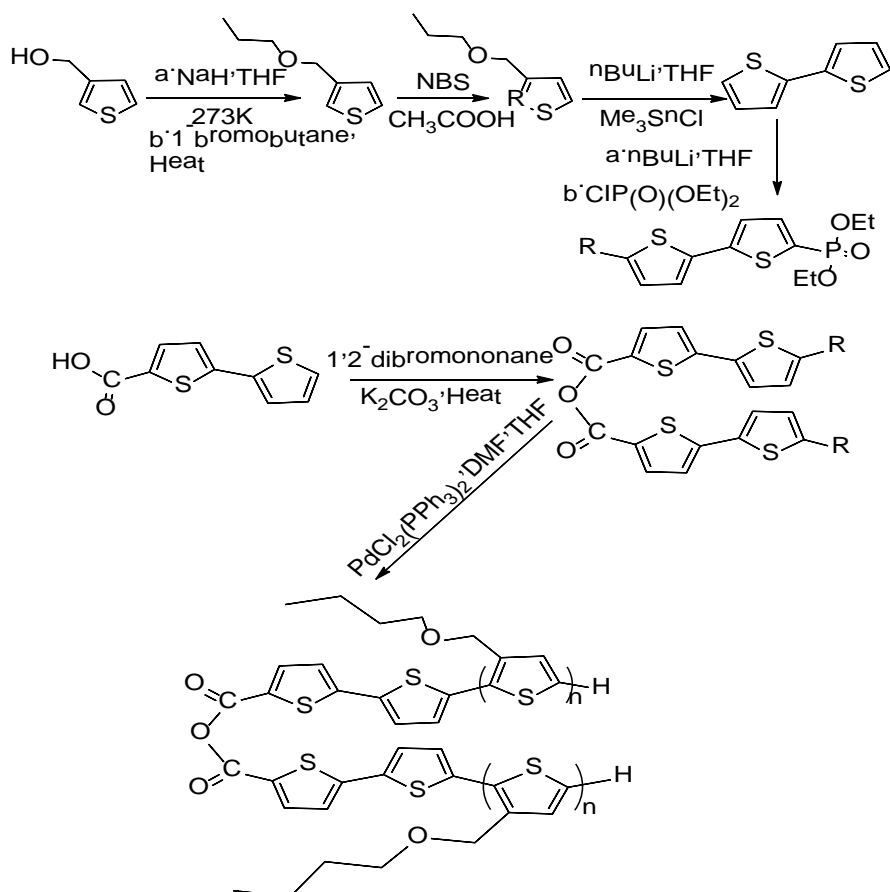


Scheme 6. Synthesis of Trisilanylene-Bridged Oligothiophenes.

Formation of oligothiophenes to act as electro-active surfactants

Solar cells based on polythiophene (Edder et al., 2003) are presently attracting much interest in the industry. Indeed, their electrical characteristics, such as large-hole mobility and absorption, make them good candidates for use as hole-conductors. Carine Edder and Jean M. J. Frechet recently utilised the conjugated polymer

poly(3-hexylthiophene) mix with CdSe nanoparticles (Kepmenkes et al., 2011) in an organic-inorganic hybrid solar cell. Furthermore, their unique molecular design, which includes a bridge at one end and a binding group (Myung et al., 2003) at the other, is anticipated to be used as electro-active surfactants for semiconducting nanoparticles or organic electronics (de Meijere et al., 2013).



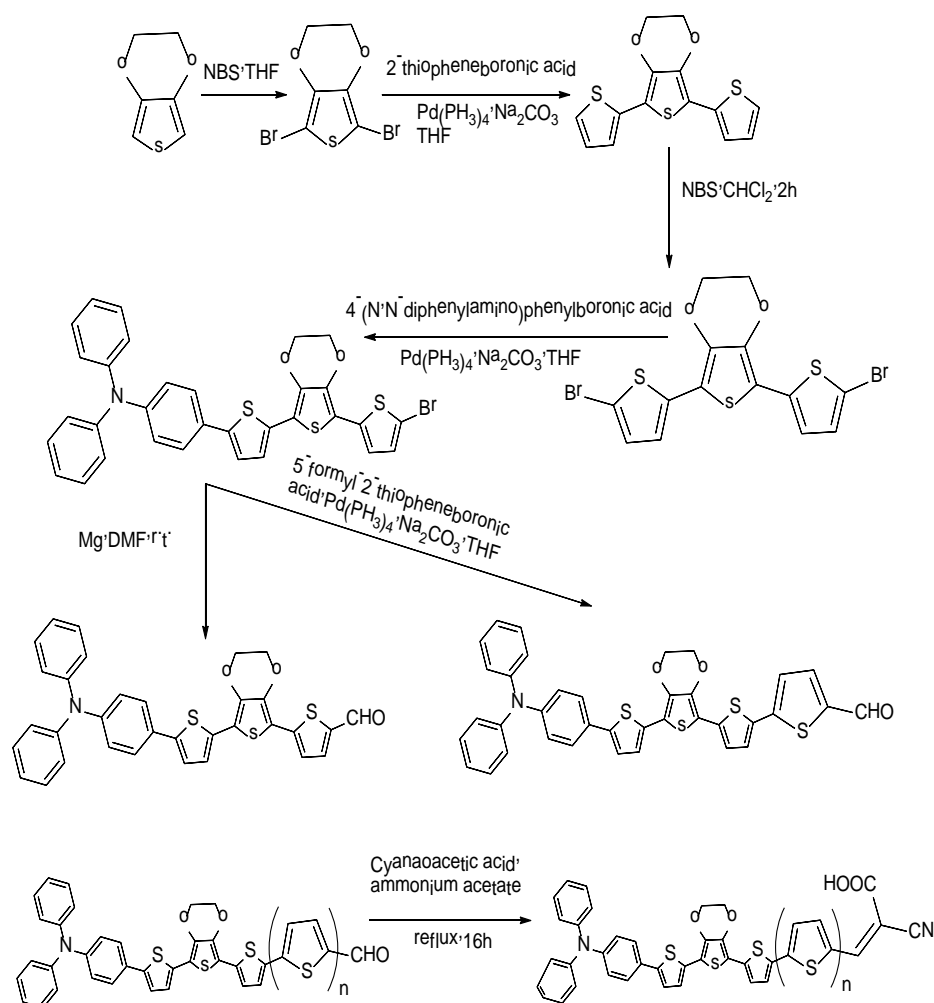
Scheme 7. Synthesis of conjugated polymer poly(3-hexylthiophene).

Synthesis of D-p-A Dyes containing Oligothiophenes

Dye-sensitized solar cells (DSSCs) (Imae et al., 2015) have attracted interest for a long time due to their high incident light conversion rate and cheap manufacturing cost. As a result, many experts have been working on developing new dyes to improve power conversion efficiency. Many kinds of D-p-A dyes have been produced since donor-p-acceptor (Hagfeldt et al., 2010) dyes with an electron donor (D) and an electron acceptor (A) connected via a p-conjugated bridge. The p-linker (Lu et al., 2013) is responsible for transporting charge or electron from the D unit to the A unit.

Because of the diversity of design (synthetically) and high coplanarity, oligothiophene is a powerful p-linker in D-p-A dyes for DSSCs.

It is also responsible for the lengthening of the p-conjugation (Liang et al., 2010). Scientists Keisuke Korai and colleagues have also synthesised a novel family of oligothiophene derivatives that include EDOT unit in part and discovered that introducing EDOT unit into oligothiophenes enhances coplanarity and improves charge transport characteristics (Ooyama and Harima, 2009). The synthesis of new D-p-A dyes using EDOT-containing oligothiophenes is described in this article.

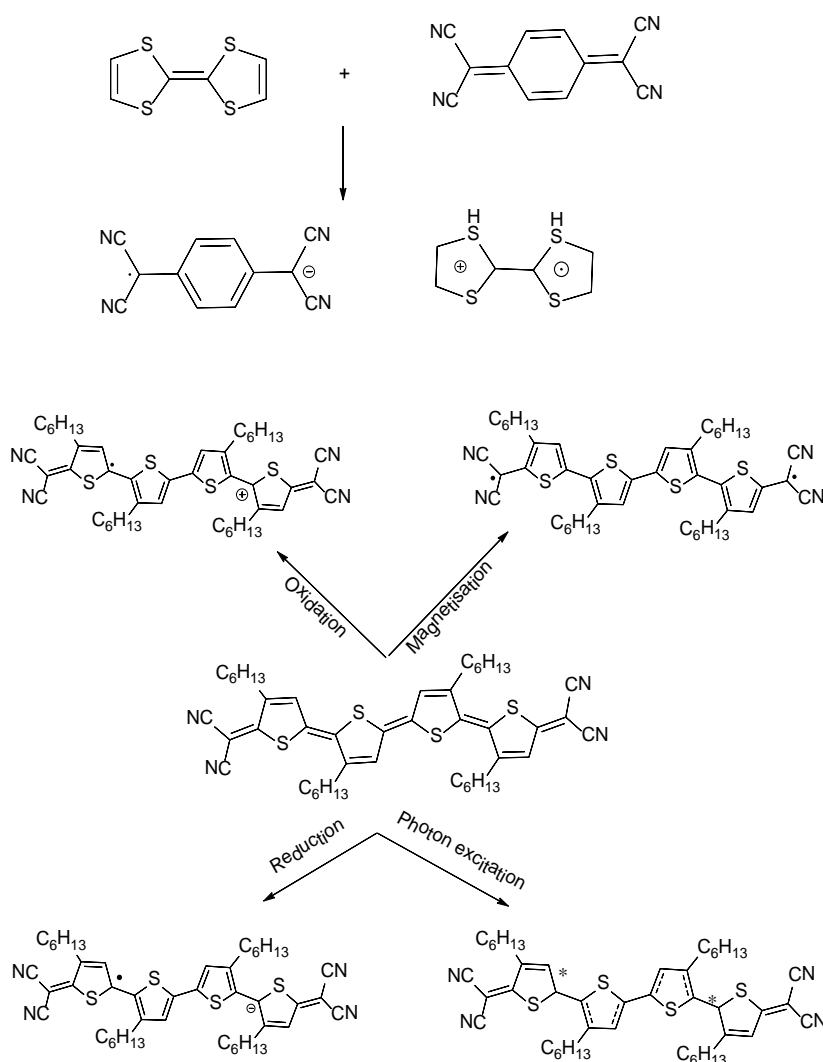


Scheme 8. Novel D-p-A dyes with EDOT-containing oligothiophenes are synthesized.

Formation of Quinoidal Oligothiophenes

The formation of conducting polymers is defined by an alternating sequence of single and double bonds (Links, 2012). (conjugated polymers). These compounds (polymers) have the unique characteristic of being changed to electrically conducting species when 'doped' (Dressler et al., 2018) with other chemicals using various processes, such as oxidation or reduction. The doping procedure results in the development of stable charged species due to the quinoidal segments at the

microscopic level (Ribierre et al., 2010). As a result, synthesising oligomers with well-defined quinoidal structures has proven difficult. Juan Casado, a scientist, updated the major work on quinoidal oligomers (Pernstich et al., 2004) as models of doped conducting polymers in this study. As a result, the researchers chose polythiophene and, by extension, quinoidal oligothiophenes as their oligomeric models. Organic electronics make extensive use of these oligothiophenes (Zade et al., 2011).

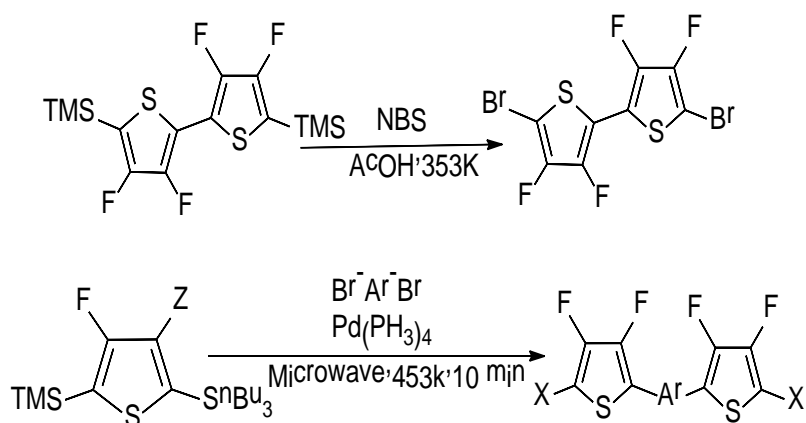


Scheme 9. Synthesis of Quinoidal Oligothiophenes and doping by different processes.

Fluorine substituted oligothiophenes

In organic semiconducting materials development of the properties of π -conjugated molecules is an important factor. Fluorine substitution on the π -conjugated system is an excellent way to lower the energies of the molecular orbital. Here, the scientists report on a systematic study of quinoidal oligothiophene (Lee et al., 2006) derivatives which contain fluorine atoms, to clarify the influence of fluorine substitution. Experimental and theoretical studies show non-covalent

interactions between S-F bonds (intramolecular) (Asoh et al., 2020) occur in these molecules and, as a result, *anti*-conformations (Osaka, 2015) form. Furthermore, electrochemical measurements show that these compounds have more excellent electron-accepting characteristics than the similar but non-fluorinated (Yuan, 2019) molecules due to the presence of fluorine. As a result, the n-type conduction occurs in organic field-effect transistors (OFETs), even under drastic conditions.

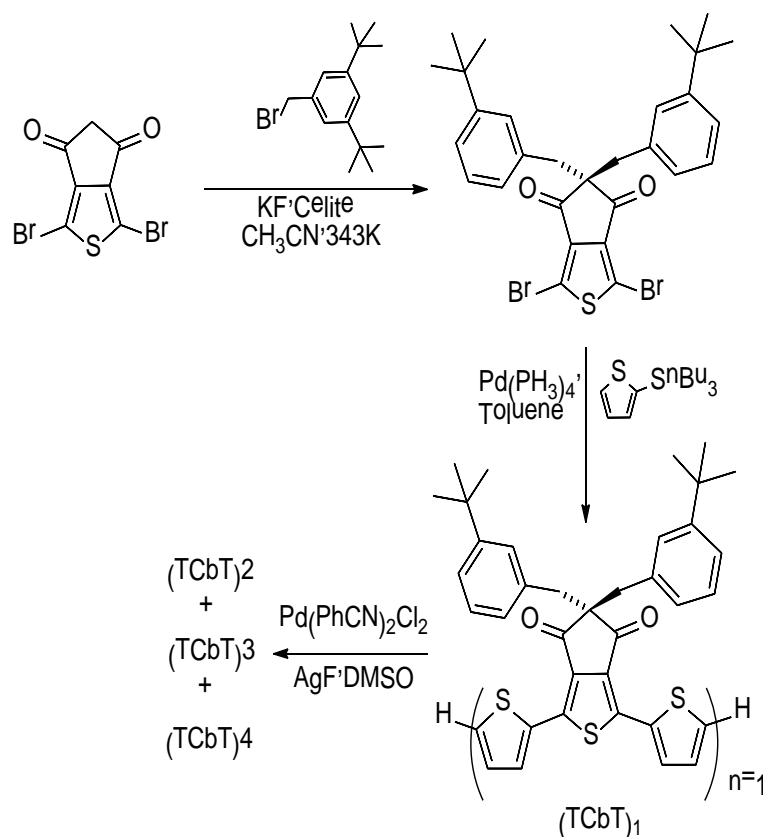


Scheme 10. Fluorine Substituted Oligothiophenes as n-type semiconductor.

Encapsulated oligothiophenes

Endou and Aso (2012) synthesised oligothiophenes with bulky bis (di-*t*-butylphenyl) (Endou and Aso, 2012) groups to create molecular wires with electron-transporting properties (Emmi et al., 1998). These features were due to their efficient conjugation, encapsulation (Shi et al. 2012) effect, and electron affinity. Oligothiophenes are structurally one of the most successful conjugated systems for electronics applications, with excellent hole-transporting characteristics and widely used optoelectronic devices. Recently, the technique has been relied on encapsulation to inhibit intermolecular p-p interactions, resulting in insulated molecular wires. Several methods have been suggested for this aim, including encapsulation with 6–8 molecules or the insertion of covalently linked bulky substituents. In recent years, Masaru Endou, Yutaka Ie, and Yoshio Aso have created encapsulated oligothiophenes and

discovered an acyclo-pentathiophene repeating unit with the bulky substituent's is beneficial to complete encapsulation. However, non-encapsulated p-conjugated molecular wires for electron transport via the LUMO orbital has mostly been restricted. It is widely known that adding electron-withdrawing groups to oligothiophenes increases electron affinity by stabilising the LUMO energy level. Di-fluorodioxo cyclo-pentathiophene has been identified as a novel electronegative unit, and oligothiophenes have been identified as n-type organic field-effect transistor materials (Mowbray, Jones, and Thygesen 2008). The conjugated backbones are successfully encapsulated while the electron-accepting characteristics are preserved by replacing the fluorine atoms in C with sterically bulky di-*t*-butylphenyl (DTBP) methyl groups. The following is a synopsis:



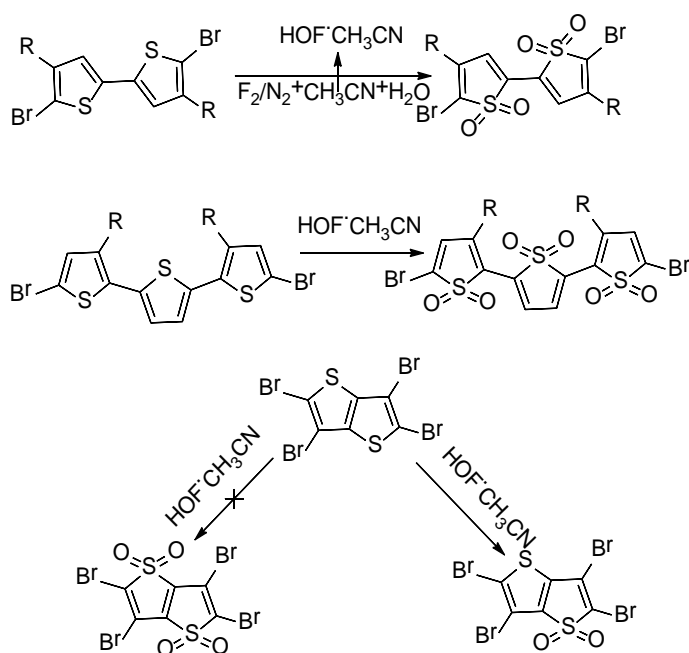
Scheme 11. Synthesis of encapsulated oligothiophenes by sterically bulky di-*t*-butylphenyl (DTBP) methyl groups.

Selective oxidation of oligothiophenes

Rozen's Reagent

In organic electronics, oxidation (Dell and Campos, 2012) happens when electrons are transferred via doping or oxygen is transferred through chemical processes, but it has a drawback in that if it is not regulated, the intended product will not be produced. Furthermore, according to Emma J, it causes charge transport disruption in field effect transistors and chemical oxidation. The regulated oxidation of thiophene in different conjugated compounds, on the other hand, affects the chemistry and the electrical

band gap, and therefore enhances the conjugation, according to Dell and Luis M. Campos. To put it another way, switching from thiophenes to their S, S-dioxide (Potash and Rozen, 2011) counterparts may help narrow the energy gap between HOMO and LUMO levels (Luo et al., 2010). However, an oxidising agent is both strong and selective enough to attack thiophenes at the S-position. Hence, the reagent is known as "Rozen's reagent" (Rozen, 2005). The optoelectronic characteristics of the oxidised thiophene-based materials are created using a stable form of hypofluorous acid, $\text{HOF} \cdot \text{CH}_3\text{CN}$.



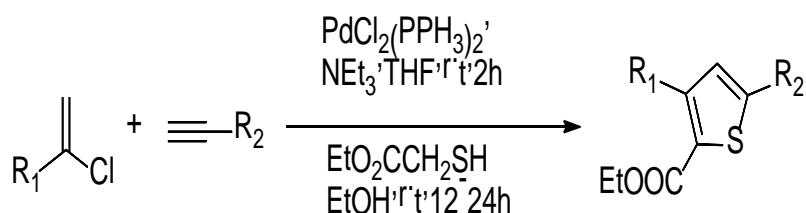
Adjacent sulphurs in fused bithiophenes can not be oxidized only one thiophene undergoes oxidation due to selectiveness.

Scheme 12. Synthesis of S,S-dioxide by Rozen's reagent(in a selective manner).

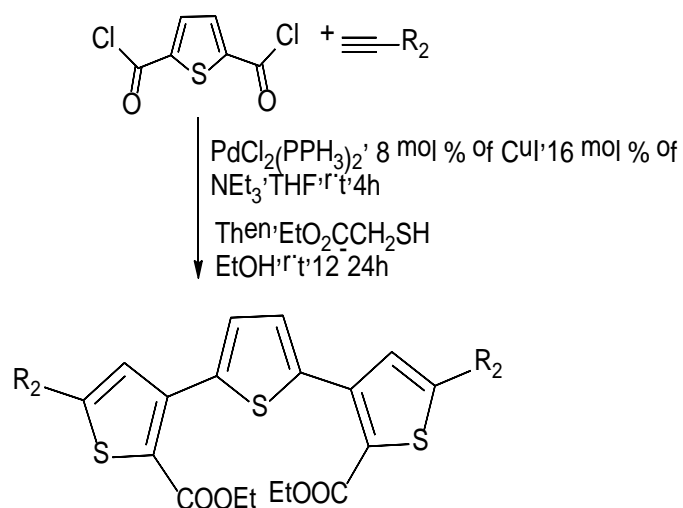
Formation of Symmetrically Substituted Ter and Quinquethiophenes

Acid chlorides and terminal dialkynes, such as aryl bis-acid chlorides (Albano and Aronica, 2020), combine to produce symmetrical terthiophenes and quinquethiophenes (very luminous) in a pseudo-five-component reaction with good yield. In recent years, Marco Teiber and his colleagues have created functional chromophores (Lee et al., 2006) and

electrophores based on the successful ideas of sequential multicomponent heterocycle synthesis. The researchers wanted to use their recently published three-component coupling-Fiessemann synthesis of 2,4-disubstituted thiophene 5-carboxylates (Teiber and Müller, 2012) to access functionalized oligothiophenes as electronic adjustable extended-system building blocks.



Scheme 13. Consecutive three-component Sonagashira alkylation-Fiessemann cyclocondensation synthesis of 2,4-disubstituted thiophene 5-carboxylate.



Scheme 14. Synthesis of symmetrically substituted ter and quinquethiophenes using a pseudo-five-component Sonogashira alkylation-FiesseImann cyclocondensation method.

Conclusion

To summarize, the synthetic methods outlined in this article have already been utilized to effectively produce a range of oligothiophenes with a unique molecular architecture based on the linking of twin oligothiophenes in the same molecule. These bridged molecules' electrical and geometric properties are being developed via structural modifications in the backbone or bridge group. In addition, organic-based electronics and solar systems are investigating using these systems as surfactants for nanocrystals and electro-active components. Once again, a range of oligothiophenes with different degrees of ring fusion was created. The impact of ring fusion on the crystal packing of these oligomers is investigated and the production of longer chain fused-ring oligothiophenes with reduced HOMO-LUMO gaps for device applications. According to our findings, oxidising thiophenes produces materials with increased electron affinity, a smaller HOMO-LUMO band gap, and higher solid-state photoluminescence efficiency. As a

result, these oxidised compounds have much potential in electronic applications.

Acknowledgement

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