Handbook of Thiophene-based Materials

Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics

IGOR F. PEREPICHKA
Centre for Materials Science
University of Central Lancashire
Preston, UK

DIMITRII F. PEREPICHKA
Department of Chemistry
McGill University
Montreal, Quebec, Canada

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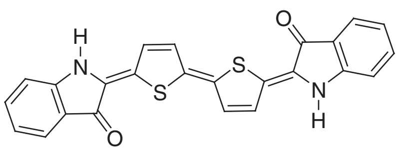
Foreword

Thiophene, the foundation of this book, had a tricky birth. It masqueraded as benzene from 1879 to 1882, when Maeyer [1] uncovered the subterfuge. It turned out that coal tar-derived benzene, when treated with isatin and sulfuric acid, produced a beautifully deep-blue precipitate, named indophenine. This pigment was claimed by Baeyer in 1879 [2] to be a qualitative test for benzene and was the product of the 'indophenine reaction'. The pigment's structure was eventually shown to consist of a quinoid form of bithiopene, shown below.



Alhough literally myriads of papers based on derivatives of thiophene have appeared since, the content of this book centers on the many things one can do once thiophene or, better, one of its derivatives has been concatenated to a macromolecule. The polythiophenes described in this book are poised to be the protagonists in the next wave of the semiconductor electronic revolution, namely organic electronics.

A simple look at indophenine reveals that it should have interesting electronic properties, particularly if incorporated in a polymer [3–6] The structure is actually more complicated than shown above, as determined in the recent past by Cava and co-workers [7] because of *cis–trans* isomerism around the double bonds between the thiophene rings and also the thiophene-to-isatin moieties. Indeed, in much more recent times, substituting 3,4-ethylenedioxythiophene for thiophene produced a small-bandgap, albeit insoluble, polymer [8].

The discussion above brings to the fore that the very first derivative of thiophene, dating back to the nineteenth century, is still fodder for scientists and engineers all the way into the twenty-first century. Just as indophenine has, this book will inspire clever synthetic chemists, materials scientists, physicists and engineers to produce wonders in energy conversion and storage and all the other applications of the current electronics revolution.

Fred Wudl
Santa Barbara
November 2008

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Preface

The discovery of high electrical conductivity in doped polyacetylene by Heeger, MacDiarmid and Shirakawa in the late 1970s spawned a multitude of interdisciplinary research activities which collectively contributed to the great success of conjugated polymers as materials enabling the development of new technologies in electronics and optoelectronics. Among all studied classes of conjugated polymers (polyacetylene, polyaniline, polypyrrole, polythiophene, polyphenylene and a large number of their derivatives and copolymers), polythiophenes display the most unique combination of efficient electronic conjugation, chemical stability and incredible synthetic versatility which allows a rainbow of properties to be accessed through substitution at the thiophene ring. Thiophene-containing polymers, copolymers and well-defined oligomers have found applications in every major technology within the field of organic electronics. Poly(3,4-ethylenedioxythiophene), PEDOT, which combines a fairly high electrical conductivity (10^2–10^3 S cm^{-1} in the doped state) with unsurpassed stability, is probably the single most industrially important organic conductor with a wide range of applications. Poly(3-hexylthiophene) (P3HT) still stands as the best p-type organic semiconductor for photovoltaics. Many other conjugated thiophene derivatives have played important and even critical roles in applications such as thin-film transistors, light-emitting diodes, electrochromic windows, photochromic devices and sensors. The popularity of polythiophenes has even spread to unexpected applications, such as in antitumor drugs.

Although no monopoly is held by polythiophenes for any of the above applications, and understanding the pros and cons for *all* conjugated materials is a must for anyone who wants to have an impact in this field, we believe that a book describing 'all you need to know' on this important class of materials can inspire the new generation of synthetic materials chemists and become a welcome reference source on the bookshelf of physicists and device engineers working in the area of organic electronics.

Ten years ago, the only predecessor of this book, *Handbook of Oligo- and Polythiophenes*, edited by Denis Fichou, was published by Wiley. Since then, a number of important advances, new approaches and new applications have emerged in thousands of peer-reviewed papers and patents. The time has come to reassess the achievements and outline the perspectives of the field. Several authors in that first handbook, other key players and emerging new names in the field have lent us their help, contributing their review chapters to the present book. It is due to their diligent efforts that we are proud to announce the most comprehensive and up-to-date resource covering all important aspects of conjugated thiophene materials.

The book is structured into four areas, describing the principles of molecular design and synthesis of oligo- and polythiophenes (Chapters 1–6), insight into their properties from the perspectives of quantum chemical calculations (Chapters 7 and 8), the fundamental aspects of the special electronic, photonic and self-assembly properties of oligo- and polythiophenes (Chapters 9–13) and, finally, the applications of thiophene-based materials in electronic and optoelectronic devices (Chapters 14–22).

Chapter 1, by Peter Bäuerle *et al.*, gives a fascinating demonstration of the synthetic versatility of thiophene which lends itself to the creativity of materials chemists. With over 400 chemical structures and over 500 citations, the chapter is undoubtedly the most comprehensive and well-structured review on the design, synthesis and properties of *oligo*thiophenes.

In Chapter 2, Richard McCullough and co-workers introduce the reader to the synthetic and characterization approaches to *poly*thiophenes and show the critical importance of regioregularity to the properties of polythiophene.

In Chapter 3, Peter Skabara reviews the emerging subclass of thiophene-based materials, fused oligothiophenes. Special attention to this subclass of oligothiophenes is well justified by, among other reasons, the very high stability of a thienothiophene building block, which makes it popular for applications in thin-film transistors and photovoltaics.

In Chapter 4, Giovanna Barbarella and Manuela Melucci reviews the synthesis and applications of thiophene-S,S-dioxide derivatives. The electron-deficient properties of these materials are of particular importance since they complement the electron-rich nature of the majority of oligo- and polythiophenes.

In Chapter 5, Michael Wolf presents hybrid-type oligo- and polythiophenes containing transition metals in their structure and reveals some special electronic properties brought about by this combination.

In Chapter 6, Tetsuo Otsubo and Kazuo Takimiya demonstrate synthetic approaches for selenium analogues of oligothiophenes and the effect of the chalcogen heteroatom on the electronic properties of these materials.

Miklos Kertesz and co-workers, in Chapter 7, gives theoretical perspectives on the question that spurred a great number of synthetic efforts – the bandgap control in polythiophene. Although a one-time holy grail of the field, a vanishingly low-bandgap polymer, is still not within reach, the concepts developed on this journey have important practical applications, e.g. in photovoltaic materials.

Michael Bendikov and Sanjio Zade, in Chapter 8, introduce the reader to the tools of quantum chemical calculation, allowing the rationalization and prediction of the structural and electronic properties of polythiophenes.

In Chapter 9, Philippe Blanchard, Antonio Cravino and Eric Levillain describe one of the most characteristic properties of polythiophenes – their rich and reversible electrochemical behavior.

In Chapter 10, Hisao Yanagi and colleagues review the studies of photonic properties in thiophene–phenylene oligomers, as related to their potential application in optical amplifiers.

The combined perspectives on the electronic and photonic properties of linear oligothiophenes and thiophene–phenylenes are further reviewed in Chapter 11 by Shu Hotta.

Self-organization of polythiophenes in liquid crystals with a multitude of morphologies and wide areas of application is the subject of the Chapter 12, presented by Kazuo Akagi.

Self-assembly of oligo- and polythiophenes in 2D monolayers, as revealed by the powerful tool of scanning tunneling microscopy (STM), is described in detail by Fabio Cicoira, Clara Santato and Federico Rosei in Chapter 13.

Stephan Kirchmeyer and colleagues, in Chapter 14, start the device application part of the book, through the introduction of the most industrially important conjugated polymer, PEDOT and showing a wide variety of its applications, such as transparent conductors, antistatic coatings, hole-injecting layers for OLEDs and photovoltaics.

In Chapter 15, Daniel Bélanger highlights the electrochemical (doping/dedoping) properties of polythiophenes through their application in supercapacitors.

Antonio Facchetti, in Chapter 16, turns to the application of the semiconducting properties of oligo- and polythiophenes and demonstrates their great potential for thin-film transistors. The chapter reviews all important advances in achieving high charge mobility in thiophene semiconductors and shows the main concepts in the design of these materials.

Iain McCulloch and Martin Heeney, in Chapter 17, review the development of the liquid crystalline thienothiophene semiconductors, and show their highly successful applications in thin-film solution-processable transistors.

The main concepts associated with the development of photovoltaic cells and the important role of polythiophene materials in this technology are introduced in Chapter 18 by Frederik Krebs and Suren Gevorgyan.

Together with our long-time colleague and friend, Hong Meng, we review the application of polythiophenes and their copolymers as electroluminescent materials for light-emitting diodes in Chapter 19.

The property of polythiophenes to change color upon the reversible oxidation/reduction process and the resulting electrochromic applications (e.g. smart windows) are the subject of the review Chapter 20 by Greg Sotzing and co-workers.

The unusual photochromic properties of thiophene derivatives are the subject of the review by Neil Branda and co-workers in Chapter 21. It is truly amazing to see the diversity of the molecular and polymer structures, and the range of photochromic properties, accessed by modification of a single building block, dithienylethene.

The book is concluded by Mario Leclerc and Hoang Anh-Ho in Chapter 22, with an account of the impressive possibilities in chemical and biological sensors brought by polythiophenes.

We cannot finish without expressing our gratitude to our authors for their hard work in writing the chapters for this book and their patience in waiting for this large project to materialize; to our referees, whose names we cannot disclose, for their altruistic help in delivering critical comments and thus improving the manuscripts; and to Alexandra Carrick and Richard Davies of Wiley for their interest and help in editing this book. Our special thanks go to Professor Fred Wudl for his advice and encouragement, and for his unique historical prospective on the field in the Foreword to this book.

Igor F. Perepichka
Centre for Materials Science
University of Central Lancashire
Preston, UK

Dmitrii F. Perepichka
Department of Chemistry, McGill University
Montreal, Quebec, Canada

List of Contributors

Acik, Muge	University of Connecticut, Storrs, CT, USA
Akagi, Kazuo	Kyoto University, Kyoto, Japan
Barbarella, Giovanna	Consiglio Nazionale Ricerche, CNR-ISOF, Bologna, Italy
Bäuerle, Peter	Ulm University, Ulm, Germany
Bélanger, Daniel	Université du Québec à Montréal, Québec, Canada
Bendikov, Michael	Weizmann Institute of Science, Rehovot, Israel
Blanchard, Philippe	Université d'Angers, Angers, France
Branda, Neil R.	Simon Fraser University, Burnaby, BC, Canada
Cicoira, Fabio	Université du Québec, Varennes, Canada
Cravino, Antonio	Université d'Angers, Angers, France
Elschner, Andreas	H.C. Starck GmbH, c/o Bayer AG, Uerdingen, Germany
Ewbank, Paul C.	Carnegie Mellon University, Pittsburgh, PA, USA
Facchetti, Antonio	Northwestern University, Evanston, IL, USA
Gevorgyan, Suren A.	Technical University of Denmark, Roskilde, Denmark
Heeney, Martin	University of London, London, UK
Ho, Hoang-Anh	Université Laval, Québec, Canada
Hotta, Shu	Kyoto Institute of Technology, Kyoto, Japan.
Invernale, Michael A.	University of Connecticut, Storrs, CT, USA
Kertesz, Miklos	Georgetown University, Washington, DC, USA
Kirchmeyer, Stephan	H.C. Starck GmbH, Leverkusen, Germany
Kobayashi, Shunsuke	National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan
Krebs, Frederik C.	Technical University of Denmark, Roskilde, Denmark
Leclerc, Mario	Université Laval, Quebéc, Canada
Levillain, Eric	Université d'Angers, CNRS, Angers, France
Ma, Chang-Qi	Ulm University, Ulm, Germany
McCulloch, Iain	Imperial College London, London, UK
McCullough, Richard D.	Carnegie Mellon University, Pittsburgh, PA, USA
Melucci, Manuela	Consiglio Nazionale Ricerche, CNR-ISOF Bologna, Italy
Meng, Hong	Du Pont Experimental Station, Wilmington, DE, USA
Mishra, Amaresh	Ulm University, Ulm, Germany

Otsubo, Tetsuo	Hiroshima University, Higashi-Hiroshima, Japan
Perepichka, Dmitrii F.	McGill University, Montréal, Canada
Perepichka, Igor F.	University of Central Lancashire, Preston, UK
Reuter, Knud	H.C. Starck GmbH, c/o Bayer AG, Uerdingen, Germany
Rosei, Federico	Université du Québec, Varennes, Canada
Santato, Clara	Ecole Polytechnique du Montréal, Montréal, Canada
Sasaki, Fumio	National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan
Sauvé, Geneviève	Carnegie Mellon University, Pittsburgh, PA, USA
Segura, José L.	Universidad Complutense, Madrid, Spain
Skabara, Peter J.	University of Strathclyde, Glasgow, UK
Sotzing, Gregory A.	University of Connecticut, Storrs, CT, USA
Stefan, Mihaela C.	University of Texas at Dallas, Richardson, TX, USA
Sud, David	Simon Fraser University, Burnaby, Canada
Takimiya, Kazuo	Hiroshima University, Higashi-Hiroshima, Japan
Tian, Yonghui	Georgetown University, Washington, DC, USA
Ubaghs, Luc	Simon Fraser University, Burnaby, Canada
Wolf, Michael O.	University of British Columbia, Vancouver, Canada
Yanagi, Hisao	Nara Institute of Science and Technology, Nara, Japan
Yang, Shujiang	George Mason University, Fairfax, VA, USA
Zade, Sanjio S.	Indian Institute of Science Education and Research, Kolkata, India

1

Functional Oligothiophene-based Materials: Nanoarchitectures and Applications

Amaresh Mishra, Chang-Qi Ma, José L. Segura and Peter Bäuerle

1.1 Introduction

Oligo- and polythiophenes are among the best investigated and most frequently used conjugated materials, in particular as active components in organic electronic devices and molecular electronics [1, 2].

Since the discovery that conjugated oligomers and polymers can be successfully implemented as active component in organic electronic devices, such as light-emitting diodes (OLEDs) and lasers, field effect transistors (OFETs), integrated circuits and solar cells (OSCs), the field of organic conjugated materials and organic electronics literally exploded in this area and a tremendous development took place. The vision to produce cheap (printable) electronics also on a large scale triggered extensive research in academia and even more in industry, expecting huge markets and many emerging companies and divisions worldwide. The most prominent and frequently used materials are doubtless poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) [3–5] in conducting and hole-transport layers of OLEDs and OSCs and also the so-called regioregular or head-to-tail coupled poly(3-hexylthiophene) (P3HT) [6–8] as a semiconductor in OFETs and OSCs. Both are rather rare examples of commercially produced conjugated polymers (Chart 1.1).

Parallel to the remarkable development of conjugated polymers with applications in the conducting and semiconducting state, a renaissance of oligothiophenes was launched in 1989 when Garnier and co-workers found that also shorter conjugated oligomers such as α-sexithiophene (6T) can be used as a material and active semiconductor in OFETs [9, 10]. Later, the implementation of structurally defined end-capped oligothiophenes (EC5T–EC7T) in OLEDs [11] was demonstrated in 1993 and of α-quinque (5T) and octithiophene (8T) in OSCs [12] in 1995 (Chart 1.2).

Furthermore, it turned out that the structurally defined and monodisperse oligomers are excellent model compounds for the corresponding polydisperse polymers which include chain length distributions, defects

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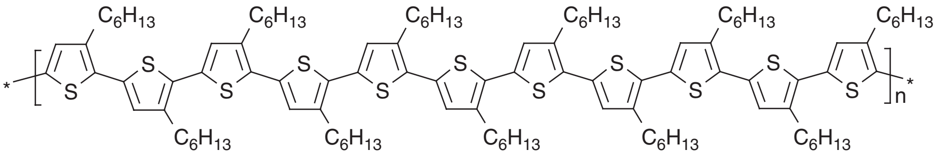
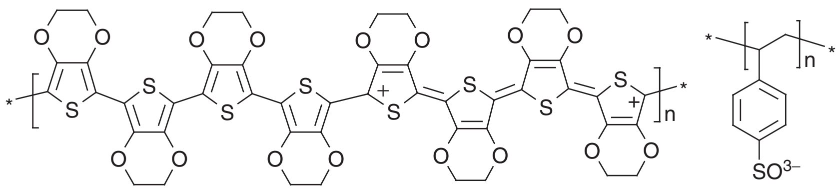
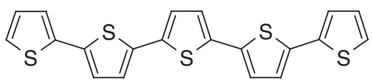


1.1 (**P3HT**)

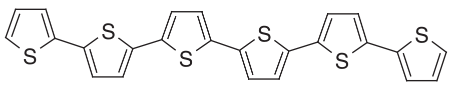


1.2 (**PEDOT:PSS**)

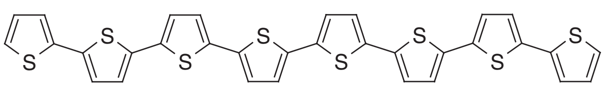
Chart 1.1



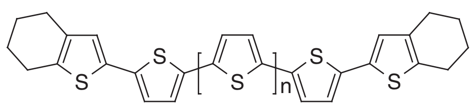
1.3 (**5T**)



1.4 (**6T**)



1.5 (**8T**)



1.6 (**EC5T-EC7T**)
(n = 1–3)

Chart 1.2

and interruptions of the conjugated chains [13]. The monitoring of various properties as a function of the chain length allows the establishment of valuable structure–property relationships and extrapolations to the polymer [14]. For nearly all basic conjugated polymers, manifold series of corresponding oligomers have been produced [2] and finally this development led to a division of organic electronics into two worlds or philosophies. On one side conjugated polymers are used which can be produced fairly simply and cheaply by polymerization of monomers and processed from solution, but include the disadvantage of less defined molecular structures, consequently resulting in less defect-free thin films. On the other side, there is the field of defined conjugated oligomers which must be synthesized and built up step-by-step and typically are processed by more costly evaporation techniques, but guarantee more defect-free layers.

As stated above, among the basic π-conjugated systems, thiophene-based materials, in particular oligo- and polythiophenes, have attracted intense interest among researchers all over the world and have actually been advanced to be the most frequently investigated structures. Two key reasons account for this development. Thiophene chemistry is well established and has been under development for a long time. There are uncountable methods to modify the core molecule [15], but more importantly, thiophenes are ideal building blocks in transition metal-catalyzed cross-coupling reactions which have been developed enormously in the past 10–20 years and nowadays provide the basis for the synthesis of most oligo- and polythiophenes [16]. In addition to the enormous and attractive potential of structural variations which allow tuning of the electronic properties over a wide range, the second reason why these materials are so successful is their outstanding chemical and physical properties. They are typically stable, both in the conducting and in the semiconducting state, and can be readily characterized by many methods. Their unique electronic, optical, redox, charge transport and self-assembling properties are intriguing, in addition to their unique arrangement and stacking properties on solid surfaces and in the bulk, which make them useful candidates for organic electronics. Finally, the high polarizability of the sulfur atom in thiophene rings leads to stabilization of the conjugated chain and excellent charge transport properties.

The field of oligo- and polythiophenes has been extensively summarized and the aim of this chapter is to cover the most recent developments and trends for oligothiophene-based materials from the perspective of molecular architecture and functionalization. Since the first report on polythiophene in 1980 [17–19] as a 1D-linear conjugated system, many smaller oligothiophenes, bi- and terthiophenes, alkylated and functionalized, have been synthesized as monomers for corresponding polythiophenes. This field has been thoroughly reviewed by Roncali [20–22], Zotti [23], Pomerantz [24], Goldenberg *et al*. [25] and Swager and co-workers [26, 27].

With the renaissance of 1D-linear oligothiophenes as the most established systems representing structurally defined model compounds and materials in their own right, at the beginning of the 1990s a period started which saw the development of many series of oligothiophenes which were mostly alkylated due to solubility reasons. The length of these molecular wires has been steadily increased over time, finally reaching Otsubo's extraordinarily long 96-mer with defined structure and highly extended conjugation, which is the 'record' to date and exceeds the length of many polythiophenes [28]. Numerous studies have been carried out investigating the relationship between the electronic properties of conjugated polymers and their chain length. Furthermore, several studies on charged species as models for the charge carriers in conducting polythiophenes have also been performed. A comprehensive review covering the development of the field up to 1998 was published by us [29] and at that time the focus was on methods of synthesis because of the modern transition metal-catalyzed C–C coupling reactions [16] that paved the way to the efficient preparation of mostly unsubstituted, alkylated and a few functionalized oligothiophenes. Roncali reviewed oligothienylenevinylenes (OTV) [30] and Spangler and He [31] and Tour [32] compiled information concerning oligothienylethynylenes (OTE) as a class of mixed systems and stiff conducting wires for molecular electronics applications. Michl *et al*. recently presented a review of molecular rods which includes oligothiophenes of all sorts [33]. Roncali recently reviewed comprehensively oligothiophenes which contain EDOT units as models for the above-described PEDOT [34]. Ozturk *et al.* focused on the synthesis of fused thienothiophenes, a class of compounds which only recently have been (re)discovered as useful building blocks in organic electronic materials [35].

Several reviews have covered varied concepts in which oligothiophenes play a major role, including those by Lemaire *et al*. on mechanisms of aryl–aryl coupling reactions [36], by Meijer *et al*. on self-organizing properties, which have progressively become an extremely important issue in designing new materials for organic electronics [37], by Fichou on structural order and X-ray structure analysis [38] and by Shirota on film- and glass-forming properties [39] Various reviews have appeared focusing on oligothiophenes as important materials in applications. Oligothiophenes in OLEDs were reviewed by us [40] and by Wudl *et al*. [41]. OFETs containing oligothiophenes were compiled by Katz *et al*. [42] and Zhu *et al*. [43]. OSCs in which oligothiophenes play an important role as donor and hole-transporting materials were reviewed by Otsubo *et al*. [44], Roncali [45] and Segura *et al*. [46]. The potential of mostly functionalized oligothiophenes to interact and detect biological molecules is the basis for sensor applications and has been documented by Swager *et al*. [27] and Barbarella *et al*. [47].

In the last 5–10 years, the number of publications on functionalized oligothiophenes, which can be considered as a third generation of advanced conjugated materials, has increased dramatically. It was recognized that with functional groups, additional properties to those of the conjugated systems can be created which are important for many applications. Furthermore, novel molecular architectures, more complicated conjugated structures and sophisticated topologies other than 1D-linear have emerged as a consequence of the increased versatility of thiophene chemistry and currently represent a most interesting and quickly spreading field of research. Since in most applications an ordering of the conjugated systems leads to improved properties, the control and understanding of the correlation between structure and self-organizational behavior also became very important. In general, an increase in dimensionality in conjugated systems can lead to different superstructures in the solid state and to multi-directional charge transport.

Therefore, at this appropriate time we review oligothiophenes with respect to functionalization and molecular architecture, and their consequences on properties and device performances were taken into account where data are available. Section 1.2 deals with 1D-linear functionalized oligothiophenes, in which the conjugated backbone either contains exclusively thiophene moieties or mixed systems, but are built up of at least a bithiophene unit. The order comes from the type of the functional groups. Section 1.3 describes fused thiophene systems which were rediscovered and widely extended to give rather band-like structures [48]. By introducing fused thiophenes as building blocks into co-oligomers and polymers, the electronic properties of the resulting conjugated system can be widely influenced. Cyclothiophenes and 2D-macrocycles containing oligothiophene units are covered in Section 1.4; these recently came into play in materials science, because they include properties of oligothiophenes but without perturbing end-effects, and show novel features due to the circular structure. In Section 1.5, recent approaches to 3D dendritic structures are described. Linear oligothiophenes decorated with classical dendrons or dendrimers which are substituted by smaller oligothiophenes have appeared on the scene. Then, in the last few years, *all*-thiophene dendritic structures came up as highly promising conjugated materials, because they represent rather stiff and shape-persistent organic functional nanoparticles. The literature included in this review is covered up to the middle of 2007.

We deliberately excluded related functionalized polythiophenes, because it would exceed the scope of this chapter. This field also has seen an enormous development and deserves a review on its own. We also did not take into account many of the structures which have already been thoroughly reviewed elsewhere in order to avoid repetition, and the reader is referred to the above-mentioned review articles.

1.2 Functionalized oligothiophenes

Oligothiophenes [1, 29, 49, 50] and their functional derivatives have been extensively studied because of their numerous applications in OLEDs [38, 40, 41], OFETs [51–54], chemosensors [27, 55], biosensors [56, 57] and electrochromic devices [58, 59], among others. In this regard, the functionalization of oligothiophenes has allowed the development of materials with specific electronic properties, which arise from both the backbone and the functional groups [60]. In this section, we will focus exclusively on the synthesis and application of functional oligothiophenes related to their self-assembly, redox activity, metal-chelating properties, molecular recognition and biological activity. In addition, a few functional polythiophenes are discussed wherever necessary and significant.

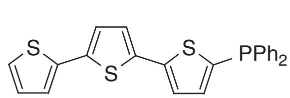
Functional oligothiophenes are generally synthesized by either oxidative homocoupling [lithiation followed by addition of $CuCl_2$ or $Fe(acac)_3$] or metal-catalyzed C–C coupling such as Kumada [61], Suzuki

[62, 63], Sonogashira [64], Stille [65] and Negishi [66] type reactions [67]. Various characterization methods such as absorption and emission spectroscopy and cyclic voltammetry are normally used to analyze the electronic properties of these materials.

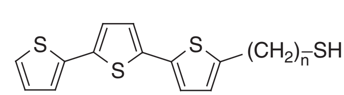
1.2.1 Oligothiophenes containing surface-active groups

Organic molecular devices which comprise conjugated molecules suitably connected to a bulk metal surface by self-assembly are of growing interest in the field of molecular-scale electronics [68, 69]. Among them, oligothiophenes are viewed as ideal systems, since they are electron rich and provide an outstanding ability to acquire positive charges and to transport them through self-assembled monolayers (SAMs) or thin films. Experimental and theoretical studies have been carried out to understand the assembly and electrical behavior of surface-bound, thiol-terminated conjugated oligomers based on thiophene and 2-thienylethynylene [70–72]. Thiols, disulfides and phosphines are known as good surface anchoring groups not only for flat surfaces, but also for nanoparticles [73]. In this respect, Wolf *et al.* reported the attachment of phosphine-tethered terthiophenes **2.1** (Chart 1.3) to Au nanoparticles which on electrochemical treatment formed a cross-linked network of π-conjugated bridges and metal nanoparticles [74, 75].

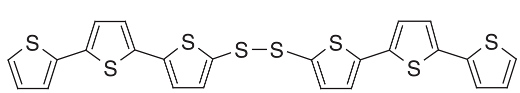
The self-assembling properties of oligothiophenes were originally reported by Liedberg *et al.* using thiol- and disulfide-functionalized terthiophenes (Chart 1.3) [76]. Undecanethiol-terminated terthiophene **2.2** ($n = 11$; 85 %) was prepared from bithiophene in seven steps and the final transformation to the thiol was carried out using thiourea. Bis(2,2′:5′,2′-terthien-5-yl) disulfide **2.3** (58 %) was prepared by lithiation of α-terthiophene with *n*-butyllithium (*n*-BuLi) and successive reaction of the monolithiated species with elemental sulfur. The formation of SAMs on Au surfaces was obtained via SH or S–S groups by solution processing. Terthiophene **2.2** showed a rapid self-assembly in minutes and anchoring via SH groups led to highly organized structures in which the tilt angle of the 3T units was 14° with respect to the surface. On the other hand, monolayers of **2.3** formed very slowly (requiring 24 h of equilibration) and showed corresponding tilt angles of 33°. A strong electronic coupling of the oligomers and the Au substrate has been proposed. Michalitsch *et al.* synthesized a series of similar alkanethiol-functionalized oligothiophenes (**2.2**; $n = 6, 8, 12$) by employing Kumada cross-coupling reactions to built up the π-conjugated part. Conversion of the terminal bromines to thiols was achieved by reaction with thiourea followed by treatment with tetraethylenepentaamine. Terthiophene **2.4** having a 7-oxanonylthiol side-chain attached to a β-position of the oligothiophene was obtained starting from 3-thiophene-ethanol in 26 % overall yield [77, 78]. Terthiophene **2.4** was adsorbed on Pt or Au surfaces to form densely packed SAMs and subsequently was electropolymerized. The resulting thin films showed high electrochemical stability [79].



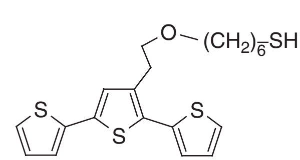
2.1



2.2: n = 6, 8, 11, 12

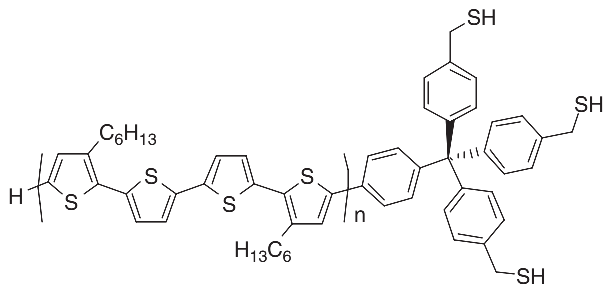


2.3

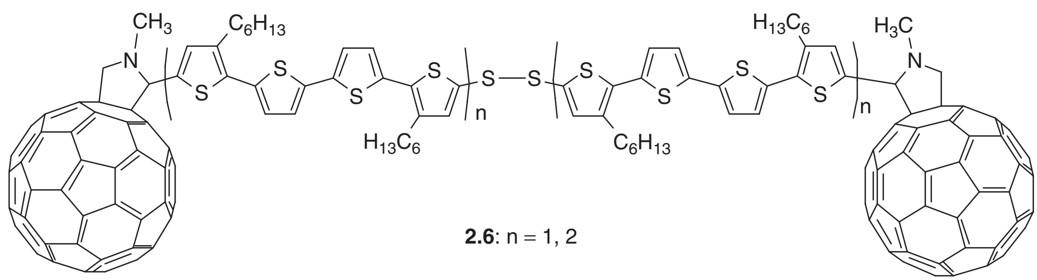


2.4

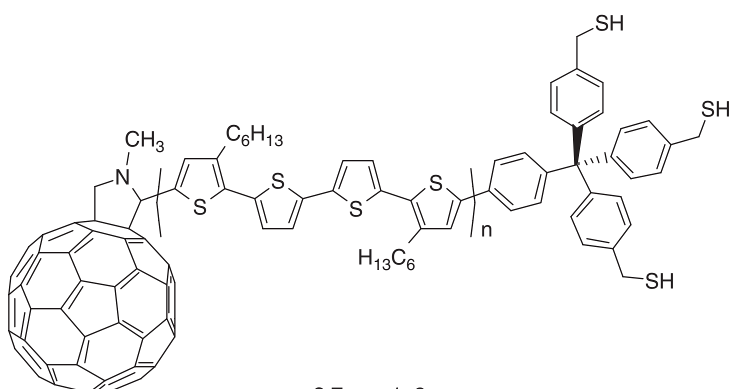
Chart 1.3



2.5: n = 1, 2



2.6: n = 1, 2



2.7: n = 1, 2

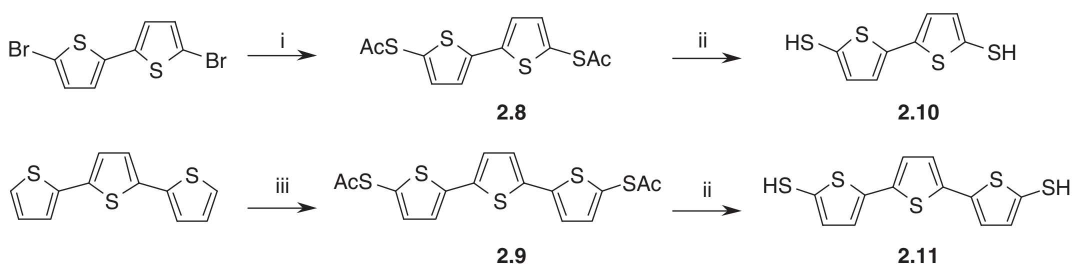
Chart 1.4

Otsubo *et al*. prepared oligothiophene dyads **2.5** which at one terminus bear a thiol-functionalized tripod consisting of a central tetraphenylmethane unit and three methanethiol groups as 'pads' (Chart 1.4) [80]. The SAM-forming compounds were prepared by Stille coupling of the stannylated oligothiophene and 4-bromophenyl-tris(4-*S*-acetylthiomethylphenyl)methane in the presence of $Pd(PPh_3)_4$ which subsequently was deprotected to the desired thiol by alkaline hydrolysis. The thiol groups acted as rigid anchors to Au surfaces and consequently the oligothiophene unit pointed outwards to promote charge transfer. The system was tested in OLEDs [Au–SAM **2.5**/TPD/Alq_3/ Mg–Ag, where Alq_3 = tris(8-quinolinato)aluminum] and an improvement in the electroluminescence (EL) was observed. The operating voltage at a luminance of 100 cd m^{-2} decreased from 9.5 V for the bare Au device to 8.5 V for the SAM **2.5** ($n = 2$) device and to

6.3 V for the SAM **2.5** ($n = 1$) device [81]. This finding revealed that the SAM of **2.5** ($n = 2$) compared with **2.5** ($n = 1$) is less compact on an Au surface due to the longer conjugated chains. The same group reported the synthesis of fullerene-functionalized oligothiophenes in which two units are coupled through a disulfide bridge (**2.6**; $n = 1, 2$) (Chart 1.4) [82]. Later, the synthesis of [60]fullerene-linked quater- and octithiophene **2.7** ($n = 1, 2$) was reported, which bears the above-described thiol-functionalized tripod **2.5** ($n = 1, 2$), allowing the formation of well-organized SAMs [83]. Photoelectrochemical measurements were performed using the cell structure Au/SAM **2.6** or **2.7**/methylviologen/Pt. In a photoelectrochemical cell the modified Au electrode acted as a working electrode and methylviologen (MV^{2+}) as an electron carrier. In comparison with a photoelectrochemical cell containing disulfide-bridged **2.6** ($n = 1$), an increase in the photoelectrochemical response and in photocurrent density by a factor of 190 has been observed for **2.7** ($n = 1$).

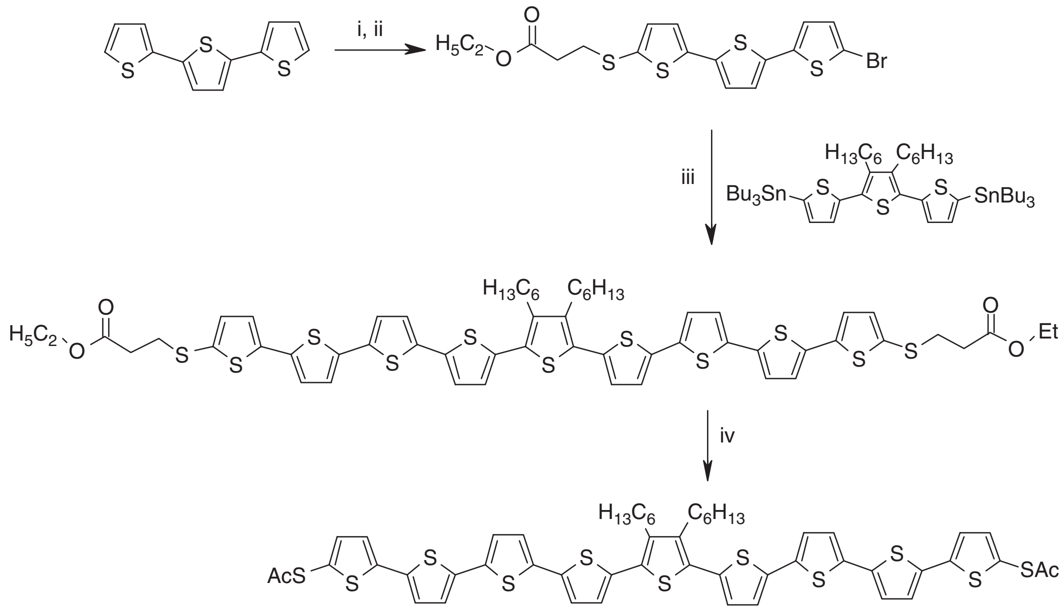
Dithiol-based bi- and terthiophenes for utilization as SAMs in molecular-scale electronics have been synthesized [84]. Functional bithiophene **2.8** was prepared by sulfurization of the Grignard reagent of 5,5′-dibromo-2,2′-bithiophene followed by acetylation. In contrast, terthiophene **2.9** was obtained by lithiation of α-terthiophene using *t*-BuLi and subsequent treatment by sulfurization and acetylation with acetyl chloride. Thiol derivatives **2.10** and **2.11** were then prepared by deprotection with ammonium hydroxide (Scheme 1.1). The self-assembling properties and molecular orientation in SAMs have been investigated by cyclic voltammetry, grazing incidence Fourier transform infrared spectroscopy (GI-FTIR), ellipsometry and contact angle measurements. A positive shift of the oxidation potential of the terthiophene unit in the SAM of **2.11** compared with that of **2.9** in solution ($\Delta E = 0.11$ V) has been discussed.

Sugawara *et al.* recently prepared the same terthiophene **2.9** and a nonathiophene **2.12** which at both termini were functionalized with thioacetate groups for attachment to gold nanoparticles [85]. Nonithiophene **2.12** was prepared in six steps starting from monolithiated α-terthiophene which was reacted with elemental sulfur, quenched with ethyl 3-bromopropionate and subsequently brominated with NBS at the other α-position. Stille-type coupling of the resulting terthiophene and a distannylated terthiophene gave the nonamer, which was transformed by acetyl chloride to thioacetylated nonithiophene **2.12** in an overall yield of 24 % (Scheme 1.2). Oligomers **2.9** and **2.12** were attached to gold nanoparticles by *in situ* removal of acetyl groups using aqueous ammonia. The self-assembling properties of the oligomers on gold nanoparticles and the resulting formation of a network structure due to the bifunctional character of the oligothiophenes were investigated by field emission-scanning electron microscopy (FE-SEM). The number of oligothiophenes attached to a nanoparticle was estimated to ∼110 for the terthiophene and ∼70 for the nonamer derivative, resulting in an average diameter of 4 nm for a nanoparticle. Conductivity measurements revealed an electron transport mechanism between the nanoparticles and π-bridging oligothiophenes, which is a prerequisite for developing molecular nanocircuits.



Reagents and conditions: (i) a. Mg/THF, b. S_8, c. AcCl; (ii) NH_4OH; (iii) a. *t*-BuLi, b. S_8, c. AcCl

Scheme 1.1



2.12

Reagents and conditions: (i) a. BuLi, b. S_8, c. ethyl 3-bromopropionate; (ii) NBS; (iii) $Pd(PPh_3)_4$; (iv) a. DBU, b. AcCl.

Scheme 1.2

Huang *et al*. prepared a series of oligothiophenes functionalized with thiocyanate groups at the termini (Chart 1.5) [86]. Terthiophene **2.13** was prepared in 89 % yield by reaction of α-terthiophene with bromine and subsequently with KSCN. 5-Bromoterthiophene was dimerized in an Ni-catalyzed homocoupling reaction followed by thiocyanation, giving sexithiophene **2.14** in 86 % yield. Nonithiophene **2.15** was built up in 72 % yield by Kumada-type cross-coupling of the Grignard reagent of 5-bromoterthiophene and 5,5′-dibromo-3′,4′-dibutylterthiophene to give the parent nonamer, which was successively brominated and transformed to the thiocyanate. Corresponding dithiol derivatives were prepared by reduction with $LiAlH_4$, which then were transferred to 2-dodecanethiol-protected gold nanoparticles (3.3 ± 1 nm) assembled between gold electrodes. By *in situ* thiol-to-thiol ligand exchange, oligothiophene dithiol-bridged gold nanoparticles were produced, finally bridging the two electrodes by means of Au–S bonds. The morphologies and current–voltage ($I-V$) characteristics of the self-assembled films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) and their photoresponsive properties have been discussed.

Soluble isocyanide-terminated oligothiophenes **2.17** up to a long heptadecamer were prepared, which in an extended form results in a length of 7 nm. Stille-type coupling of 2-bromo-5-(4-formamidophenyl)thiophene with stannylated quaterthiophene followed by bromination yielded **2.16** ($n = 4$) as intermediate building block. Corresponding higher oligomers **2.16** ($n = 8, 12, 16$) were prepared by cycles of Stille-type coupling and bromination. Isocyanides **2.17** ($n = 4, 8, 12, 16$) were finally obtained by dehydration of the corresponding formamides **2.16** using triflic anhydride under basic condition (Scheme 1.3) [87]. Oligothiophenes **2.17** ($n = 4, 8, 12, 16$) were characterized by UV–Vis, fluorescence and cyclic voltammetric (CV) measurements. With increase in conjugation length, the absorption maximum shifts from 409 to 430 nm