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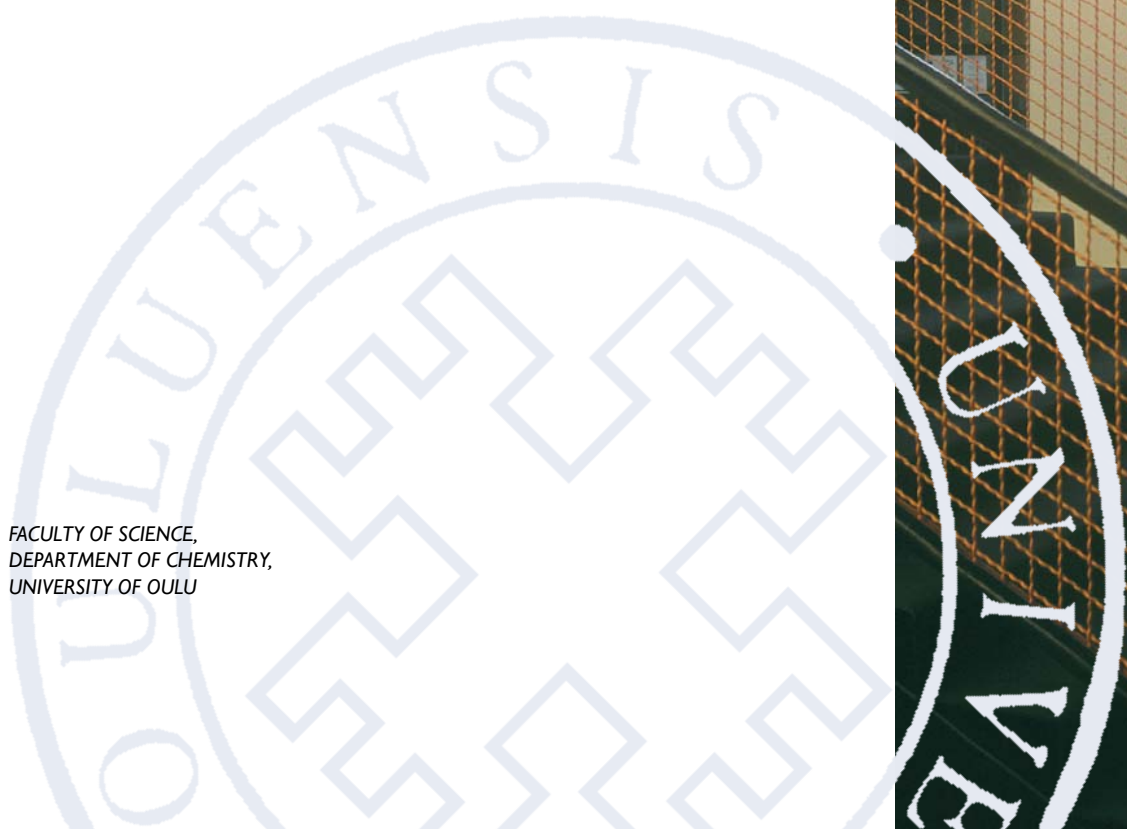
Terhi Alaviuhkola

AROMATIC BORATE
ANIONS AND THIOPHENE
DERIVATIVES FOR SENSOR
APPLICATIONS

FACULTY OF SCIENCE,
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF OULU

A

SCIENTIAE RERUM
NATURALIUM



ACTA UNIVERSITATIS OULUENSIS
A Scientiae Rerum Naturalium 497

TERHI ALAVIUHKOLA

**AROMATIC BORATE ANIONS AND
THIOPHENE DERIVATIVES FOR
SENSOR APPLICATIONS**

Academic dissertation to be presented, with the assent of
the Faculty of Science of the University of Oulu, for public
defence in Auditorium IT115, Linnanmaa, on December
8th, 2007, at 12 noon

OULUN YLIOPISTO, OULU 2007

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Acta Univ. Oul. A 497, 2007

Supervised by
Professor Jouni Pursiainen

Reviewed by
Professor Jouko Kankare
Professor Jouko Vepsäläinen

ISBN 978-951-42-8656-8 (Paperback)
ISBN 978-951-42-8657-5 (PDF)
<http://herkules.oulu.fi/isbn9789514286575/>
ISSN 0355-3191 (Printed)
ISSN 1796-220X (Online)
<http://herkules.oulu.fi/issn03553191/>

Cover design
Raimo Ahonen

OULU UNIVERSITY PRESS
OULU 2007

Alaviuhkola, Terhi, Aromatic borate anions and thiophene derivatives for sensor applications

Faculty of Science, Department of Chemistry, University of Oulu, P.O.Box 3000, FI-90014
University of Oulu, Finland
Acta Univ. Oul. A 497, 2007
Oulu, Finland

Abstract

This study was part of a project targeted at developing chemical sensors for organic cations and metal ions by exploiting the interactions between cations and anionic borate derivatives. As well, the chemical synthesis of thiophene monomers with charged or neutral ion-recognition sites was investigated.

The primary task in the first part of the work was to prepare anionic receptor molecules based on synthesized borate derivatives and study their complexation with *N*-heteroaromatic and tropylium cations. The complexation was studied in solution by ^1H NMR and ESIMS techniques and in solid state by X-ray crystallography. Crystal structures showed evidence of weak noncovalent interactions—hydrogen bonding, cation $\cdots\pi$ interactions, and π -stacking. In addition, the crystal structure of the alkali metal complex of tris[3-(2-pyridyl)pyrazolyl]hydroborate was determined. Stability constants of borate complexes were measured by ^1H NMR titration in methanol/acetonitrile (1:1) solution at 30 °C. Various derivatives of aromatic borate anions synthesized within this project, some commercially available derivatives, and two neutral carriers containing aromatic anthryl groups were also studied as recognition sites for aromatic cations where *N*-methylpyridinium was used as primary ion in PVC membrane-based all-solid-state ion sensors. The results showed that borate derivatives offer new possibilities for molecular recognition by ion-selective electrodes (ISEs).

The aim of the second part of the study was to develop chemical ion sensor materials where the ion-recognition unit and the charge-compensating ion are covalently coupled to the backbone of a conductive polymer. Sulfonated thiophenes were used as doping ions for the fabrication of Ag^+ -ISEs. More than 15 differently substituted monomers were synthesized. The materials differed with respect to the receptor unit, extent of oxidation, counteranion, and length of the chain.

Keywords: borates, ion-selective electrode, noncovalent interactions, supramolecular

Acknowledgments

The present study was carried out in the Laboratory of Physical Chemistry at the Department of Chemistry, University of Oulu. Funding was provided by the Graduate School of Inorganic Materials, the Finnish Funding Agency for Technology and Innovation (TEKES), the Alfred Kordelin Foundation, and the University of Oulu.

The begin with, I would like to thank my supervisor, Dean of the Faculty of Science, Professor Jouni Pursiainen, for proposing the subject of my research and giving me the opportunity to perform this study. He has been most patient through all the ups and downs of my research.

I am indebted to referees Professor Jouko Kankare and Professor Jouko Vepsäläinen for carefully reviewing the manuscript and providing valuable comments and feedback. The English language was revised by Kathleen Ahonen, to whom sincere thanks for her contribution.

Many thanks go to my co-authors at Åbo Akademi University and the University of Jyväskylä and to collaborators at the University of Oulu. I am most grateful to the staff of the Department of Chemistry for the support they gave. Special thanks are owing to Docent Perttu Permi for reading through my thesis and offering help whenever I approached him with a problem, to Ritva Juvani (Phil.Lic.) for her comments on my thesis, and to Maarit Risto (Phil.Lic.) for her contributions. Terhi Suopajarvi, my office-mate and partner-in-crime during these past several years is warmly thanked for her friendship.

Finally I would like to express my gratitude to my family members and friends, in Oulu and elsewhere, for maintaining my humor even when none of the clouds seemed to contain silver linings.

Oulu, November 2007

Terhi Alaviuhkola

Symbols and abbreviations

Bu	butyl
C	complex
CD ₃ CN	deuterated acetonitrile
CD ₃ OD	deuterated methanol
CDCl ₃	deuterated chloroform
CPISE	conductive polymer-based ISE
CV	cyclic voltammetry
δ	chemical shift
d	doublet (spectral)
D ₂ O	deuterated water
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide
DEPT	distortionless enhancement by polarization transfer
DOS	bis(2-ethylhexyl)sebacate
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EDOT	3,4-ethylenedioxythiophene
EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz crystal microbalance
FAB	fast atom bombardment
ESI	electrospray ionization
FTIR	Fourier transform infrared spectroscopy
G	guest
GC	gas chromatography
H	host
HMBC	heteronuclear multiple bond correlation
Im ⁺	imidazolium cation
ISE	ion-selective electrode
J	coupling constant (in NMR spectroscopy)
K	stability constant
m	multiplet (spectral)
Me	methyl
MS	mass spectrometry
<i>N</i> -MePy ⁺	<i>N</i> -methylpyridinium cation
NMR	nuclear magnetic resonance
DMF	dimethylformamide

OMe	methoxy
<i>o</i> -NPOE	2-nitrophenyl octyl ether
PEDOT	poly(3,4-ethylenedioxythiophene)
PEDT	poly(3,4-ethylenedioxythiophene)
Ph	phenyl
ppm	parts per million
ProDOT	3,4-propylenedioxythiophene
PSS ⁻	poly(styrenesulfonate) anion
PVC	polyvinylchloride
Py	pyridine
Py ⁺	pyridinium cation
q	quartet (spectral)
r ²	regression correlation
s	singlet (spectral)
SCISE	solid-contact ISE
t	triplet (spectral)
T	temperature
TBA ⁺	tetrabutylammonium cation
TBB ⁻	tetrabutylborate anion
TBSCl	<i>tert</i> -butyldimethylsilyl chloride
THF	tetrahydrofuran
TMA ⁺	tetramethylammonium cation
TMS	tetramethylsilane
TPB ⁻	tetraphenylborate anion
TpCIPB ⁻	tetrakis(4-chlorophenyl)borate anion
TpFPB ⁻	tetrakis(4-fluorophenyl)borate anion

List of original papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. Some unpublished results are included.

- I Bobacka J, Alaviuhkola T, Hietapelto V, Koskinen H, Lewenstam A, Lämsä M, Pursiainen J & Ivaska A (2002) Solid-contact ion-selective electrodes for aromatic cations based on π -coordinating soft carriers. *Talanta* 58 (2): 341–349.
- II Alaviuhkola T, Bobacka J, Nissinen M, Rissanen K, Ivaska A & Pursiainen J (2005) Synthesis, characterization, and complexation of tetraarylborates with aromatic cations and their use in chemical sensors. *Chemistry–A European Journal* 11 (7): 2071–2080.
- III Nissinen M, Alaviuhkola T, Rissanen K & Pursiainen J (2006) Crystal structure of potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate. *Journal of Chemical Crystallography* 36 (12): 863–868.
- IV Mousavi Z, Alaviuhkola T, Bobacka J, Latonen R-M, Pursiainen J & Ivaska A (2007) Electrochemical characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with sulfonated thiophenes. *Electrochimica Acta*. In press.

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1 Introduction

Supramolecular chemistry is one of the fastest growing fields of experimental chemistry. In contrast to molecular chemistry, which is predominantly based on the covalent bonding of atoms, supramolecular chemistry can be defined as the chemistry of molecular assemblies and of intermolecular bonding [1]. It is chemistry beyond the molecule, the chemistry of noncovalent bonds, or nonmolecular chemistry. Specific applications are molecular recognition, which is the interest here, catalysis, and transport [1,2,3]. Intermolecular interactions can be classified as ion–ion interactions, ion–dipole interactions, dipole–dipole interactions, hydrogen bonding, cation $\cdots\pi$ interactions, π -stacking, Van der Waals forces, close packing in the solid state, and hydrophobic interactions.

Noncovalent interactions play a dominant role in modern material design [4]. The possibility of achieving unique materials with defined functions, e.g., with the electronic properties of semiconductors and the lightness of weight and processability of organic polymers, has created much excitement over the last few decades [5,6]. A good example is the search for molecules that can be used for the construction of sensing membranes–recognition devices that selectively respond to a particular analyte (target ion) rather than to other ions that may be present. To achieve this, the recognizing species must be designed to match the binding properties of the target analyte as closely as possible. In addition, the host–guest interaction must trigger an observable response in the measuring device. Joining the binding increments, for instance to a conjugated polymer backbone, to obtain selective and reversible ion sensors links the fields of supramolecular chemistry and chemical sensors closely together. The complexation of transition metals with crowns, cryptands, or spherands is a classical example of supramolecular chemistry.

1.1 Borates

Ternary boranes have a planar sp^2 -hybridized valence state with a vacant p orbital perpendicular to the plane of the molecule. The availability of three electrons, which can contribute to covalent bonding involving the four orbitals s, p_x , p_y , and p_z , confers a range of properties on B leading, for example, to electron-pair acceptor behavior (Lewis acidity) toward a wide variety of bases. In this way, four-coordinate species with approximately tetrahedral structures are formed.

Boron also completes its octet by forming both anionic and cationic complexes. The former include such species as BF_4^- , $\text{HB}(\text{OR})_3^-$, and $\text{B}(\text{C}_6\text{H}_5)_4^-$.

Borates are anions in which the negative charge is associated with electrons in bonding orbitals. There are numerous examples of anionic BR_4 derivatives. All the R-groups can be replaced by substituents, varying from alkyl or alkoxy chain and aryl ring to hydrogen or halogen atom. The synthesis of borate structures has nevertheless stressed hydroborates. Tetrahydroborate complexes are known for a large number of main group, transition metal, and actinide elements [7]. Thousands of reports concerning the use of these compounds as reducing agents in organic and inorganic synthesis can be found in the literature [8]. In similar manner, alkyl-, alkoxy-, or aryl-substituted borohydrides are used as selective reducing agents [9,10,11,12]. The reactivity of these derivatives and the stereochemical course of the reactions are strongly influenced by the nature of the alkyl substituent on boron. The present study focuses on arylborate derivatives.

Tetraphenylborate, the simplest tetraarylborate, was introduced in analytical chemistry in the 1940s. At that time it was used for the precipitation of monopositive cations such as potassium, rubidium, cesium, and quaternary ammonium compounds [13]. Tetraphenylborate has been widely used as counterion in metal complexes. Borate anion can interact with metal centers via its phenyl groups. Not surprisingly, a myriad of crystal structures of tetraphenylborate complexes have been published. In cation $\cdots\pi$ interactions, the cations are strongly attracted to the π face of benzene and other aromatic structures. The face of a benzene ring provides a partial negative charge, which may be quite substantial, and the ring interacts favorably with cationic structures. The term cation $\cdots\pi$ interaction has been proposed to describe all such effects. It is meant to be a descriptive term, and emphasizes the essential nature of the interaction. The definition of a cation $\cdots\pi$ interaction excludes complexes of transition metals such as Ag^+ or Fe^+ with benzene and related π systems. The bonding in such systems is clearly quite different in nature because interactions are with d-orbitals on the metal. Although tetraphenylborates have been used as precipitating reagents in analytical chemistry for a long time, numerous studies also exist on other substituted borates that form salt-like precipitates [14]. In contrast, not much interest has been shown in borate complexes containing organic cations as guest molecules, although a variety of borates substituted with aryl groups have been synthesized [15,16].

Numerous examples of N-H $\cdots\pi$ and O-H $\cdots\pi$ bonds to aromatic π systems in organic ammonium tetraphenylborates have been reported providing a

classification that could serve as a reference for X-H $\cdots\pi$ (arene) bonds in general [16]. The structures contain a variety of normal, bifurcated, and trifurcated hydrogen bonds to the phenyl groups of the anion. The crystal structures of *cis*-2,2'-bipyridinium and 1,10-phenanthroline tetraphenylborates show similar hydrogen bonding, and crystal structures of the latter also significant $\pi\cdots\pi$ stacking interactions [17]. Moreover, investigations of complexation of tetraphenylborate with organic *N*-heterocyclic cations indicate that weak noncovalent interactions, such as C-H $\cdots\pi$ and N-H $\cdots\pi$ hydrogen bonds (Fig. 1) and π -stacking, are the principal intermolecular forces between aromatic π systems of anion structure and organic cations in the crystalline state [18].

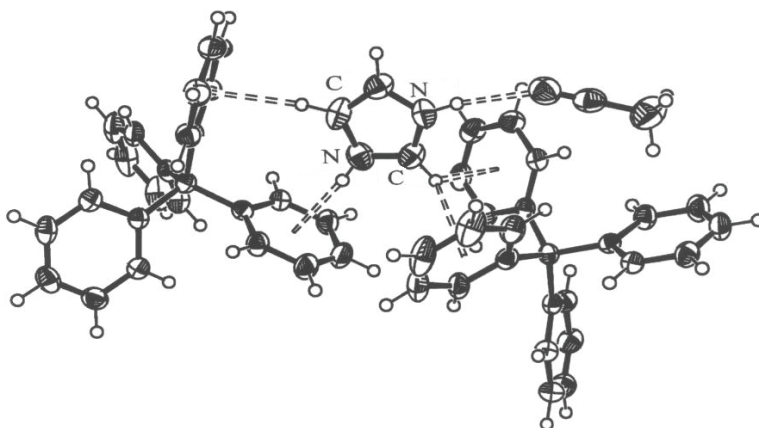


Fig. 1. Crystal structure of imidazolium tetraphenylborate complex. Imidazolium is located between two hosts and interacts with them via C-H $\cdots\pi$ and N-H $\cdots\pi$ interactions [18].

Aromatic groups, cations, and metal ions that have the ability to engage in $\pi\cdots\pi$ stacking, hydrogen bonding, or cation $\cdots\pi$ interactions are also of considerable importance in ionophore–aromatic cation interactions. The phenyl groups of tetraphenylborate derivatives are potential π -coordinating sites for aromatic cations. Tetraphenylborate derivatives (Fig. 2) have been used in ion-selective electrodes (ISEs) to reduce the anionic interference arising in the presence of lipophilic anions [19]. Although they cannot form specific and strong ion-pairs owing to their shielded negative charge, they still seem to play an active role as complexing agents in addition to bringing negative charge to the sensor surface. It was recently shown that the Hg²⁺ interference on Ag⁺-ISEs can be reduced by six orders of magnitude by replacing tetrakis(4-chlorophenyl)borate,

TpCIPB⁻, with a weakly coordinating carborane as the anionic additive in the ion-selective membrane [20]. The significance of the tetraphenylborate derivatives as lipophilic anionic sites has been especially great in the area of ion-selective electrodes, but also important in the field of the optical sensors. In sum, complexation of organic cations is an important area of supramolecular chemistry having applications in synthetic, analytical, and industrial fields.

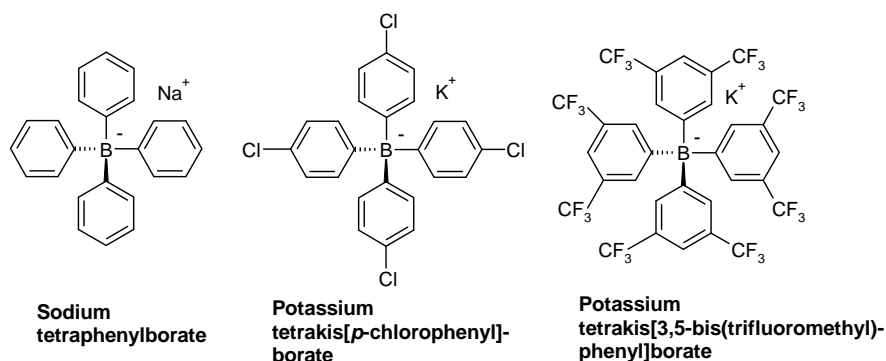


Fig. 2. Tetraphenylborate derivatives used in ISEs.

Properties of borate derivatives have been studied in our laboratory in a project targeted at determining their influence on the selectivity and sensitivity of ion-selective electrodes. The research has been carried out in close collaboration with the Ivaska laboratory at Åbo Akademi University, where the borate compounds were incorporated as ion-recognition sites (receptors, ionophores) in potentiometric sensors for cations and metal ions. The X-ray crystallographic work was carried out at the University of Jyväskylä by Professors Nissinen and Rissanen. The results have been promising. Modifications to the borate structure have been found to influence the selectivity of potentiometric ion sensors. In the present work, the complexation chemistry of anionic borate derivatives was mostly studied with heterocyclic cations. Sections 2.2.1, 2.2.2, and 2.3 describe the syntheses and characterization of the borates and their complexes and the stability constant measurements, while sections 3.1, 3.2, and 3.4.1 present and discuss the results.

1.2 Thiophenes

Thiophene has a planar pentagonal structure in which the four carbons and the sulfur form an sp^2 -hybridization. The remaining p-orbitals on each atom overlap to form a π -molecular system. The six π -electrons give the molecule its aromatic character. The second lone pair on the heteroatom is perpendicular to the π system of the ring. Thiophene is usually first substituted at the 2- and 5-positions and, if these are occupied, the 3- and 4-positions. Thiophenes occur as structural units in many natural molecules finding application in the flavor and pharmaceutical industries. Thiophene-based functional polymers are an important class of conductive polymers.

The modern era of conductive polymers began at the end of the 1970s when Heeger and MacDiarmid discovered that polyacetylene synthesized by Shirakawa's method could reach extremely high electrical conductivities after treatment with oxidizing agents [21,22,23,24]. It was this discovery that gave Heeger, MacDiarmid, and Shirakawa the Nobel Prize in Chemistry in 2000.

Polyacetylenes and polyanilines are highly conductive materials in the doped state. Isoelectronic poly(thiophene) and poly(pyrrole) derivatives rank among the most widely studied conductive polymers (Fig. 3). Conductive polymers are excellent ion-to-electron transducers, which are essential building blocks in electrochemical ion sensors. The research on conductive polymers has basically fallen into three areas: the establishment of a fundamental basis for describing the charge transport, the tailoring of conductive polymers with desired electrical and mechanical properties, and the development of novel applications based on the unique properties of these materials. As one result of these investigations, the selectivity and sensitivity of potentiometric sensors have been improved. Conductive polymers are under intensive study today. They can be used in applications extending from antistatic coatings and corrosion protection to sophisticated molecular devices, selective modified electrodes, and various sensors [5,25,26].

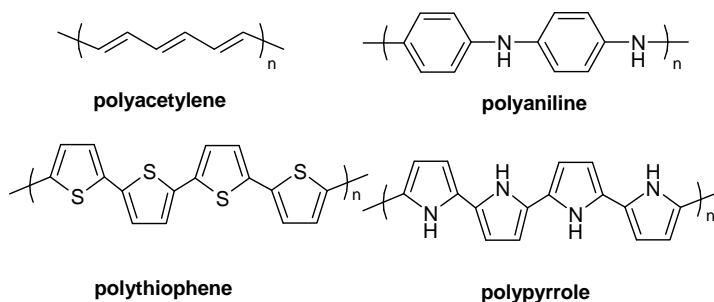


Fig. 3. Examples of conductive polymers.

The addition of side chains to the aromatic backbone not only enables easier processing of the polymeric materials but may also modify the electronic properties of the polymers. Control over the molecular conformation and supramolecular organization of π -conjugated polymers provides the conditions for fine-tuning of their electrical and optical properties [27]. Several publications describe thiophene derivatives containing no chemically reactive groups because such substituents are also known to interfere with the polymerization reaction. All known conjugated polymers possessing molecular recognition properties can be divided into the following generalized structures: 1) structures in which the receptor unit is fused to the signalling conjugated polymer backbone (i.e. the structure possesses a conformationally flexible chain receptor), 2) structures in which a receptor or redox substituent, or both, are incorporated into the chain, and 3) structures in which the receptor is a counterion inserted into the polymer film, with no chemical link to the polymer. While unsubstituted polythiophenes are known to be insoluble, alkyl or aryl chain substitution at the 3-position induces solubility. Furthermore, the presence of alkoxy chains decreases the steric hindrance in the vicinity of the main chain.

One of the most widely investigated alkoxy-substituted polythiophenes is the polymer derived from 3,4-ethylenedioxythiophene, also known as PEDT or PEDOT [28,29]. The monomer (EDOT) has been known since 1938. Appending an alkylenedioxy bridge across the 3- and 4-positions adds electron density to the aromatic ring, reducing both the monomer and the polymer oxidation potentials, and leading to the formation of highly stable conductive polymer.

The present work was targeted at adding selectivity to the conductive polymers of chemical sensors by covalently attaching supramolecular groups to act as ion-recognition sites, or ionophores. The potential of the above-mentioned

attractive, highly selective, host–guest interaction between receptor unit and analyte was not fully exploited in this work. The key idea was, through study of thiophene-based conductive polymers bearing molecular recognition groups, to increase our understanding of the mechanism of molecular recognition and signal transduction in functionalized conjugated polymers.

A specific, tailored attractive interaction between the receptor and the incoming analyte would increase the selectivity of chemical sensors enormously. Attractive interactions suggest a highly promising approach to ion-selective electrodes. The knowledge gained during this study will be used to develop chemical sensors for analytical applications with even more selective supramolecular units. Despite the many innovations during the last decade, the research based on conjugated polymers with supramolecular recognition sites is still at an early stage.

Thiophene derivatives were synthesized and characterized in our laboratory. The group at Åbo Akademi University tested the electropolymerization properties of these compounds and investigated the possibility of utilizing them as ionophores in potentiometric sensors. Sections 2.2.3–2.2.5 describe the syntheses and characterization of the 3-substituted thiophenes and 3,4-ethylenedioxythiophenes, and sections 3.3 and 3.4.2 the results and discussion.

1.3 Chemical sensors

A chemical sensor is a device that converts a chemical state into a measurable signal. The sensing process involves molecular recognition of a chemical species and transduction of the chemical information into a measurable signal. [30,31] Molecular recognition is basically a process whereby an electroactive receptor (host) interacts with an analyte (guest) to form a supramolecule. One of the first examples of molecular recognition using conjugated polymers was reported at the end of the 1980s for oxyethylene-substituted polythiophene derivatives [32].

Electrochemical sensors are one group of chemical sensors, and potentiometric ion sensors, which are of interest here, are an important subgroup of electrochemical sensors [33]. Conductive polymer can be electrochemically deposited on a solid electronic conductor and thereafter coated with an ionophore-based ion-selective membrane [30]. The solid-contact K^+ -selective electrode, in which the internal reference electrode and solution are replaced by a layer of conductive polymer (see Fig. 4), demonstrates the principle of the solid-contact ion-selective electrode (SCISE) [34].

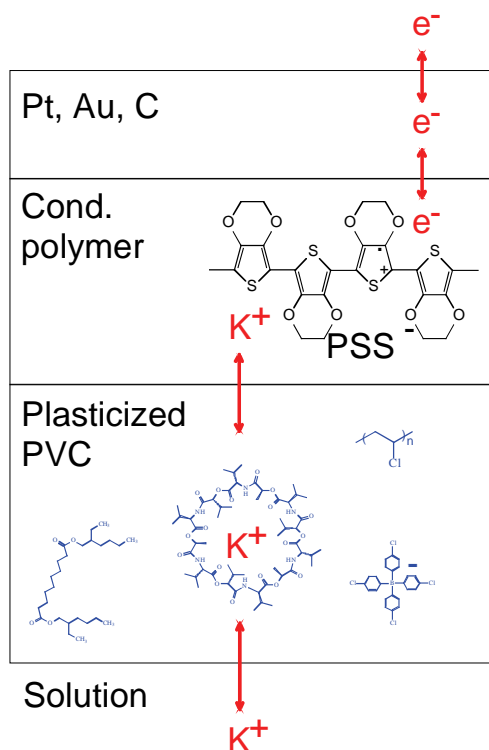


Fig. 4. Solid-contact K⁺-ISE based on plasticized PVC containing valinomycin as the ionophore. PEDOT doped with immobilized poly(styrenesulfonate) (PSS⁻) works as the ion-to-electron transducer [34].

The ion-selective part is a PVC-based K⁺-sensitive membrane. Valinomycin is used as the potassium-selective ionophore, bis(2-ethylhexyl)sebacate as a plasticizer, and tetrakis(4-chlorophenyl)borate as the charge-balancing lipophilic anion. The solid-contact ISE is constructed with use of poly(3,4-ethylenedioxythiophene) as solid-contact material, where the positive charge is compensated with the poly(styrenesulfonate) anion, PSS⁻. Charge transfer between the ion-selective membrane and the conductive polymer takes place by K⁺-ion transfer. Between the substrate, which is an electronic conductor, and the conductive polymer, charge transfer takes place by electron transfer.

The idea is that selective sensors based on specific molecular recognition detect a particular species in the presence of many other species. Strong molecular interactions will often result in irreversible binding, which makes the

sensor a single-use device. Development of chemical sensors that are both selective and reversible requires optimization of the molecular recognition sites, which links this research closely to supramolecular chemistry.

1.4 Aims of the work

Host–guest chemistry, as mentioned above, involves complexes that are composed of two or more molecules or ions held together by hydrogen bonding, π -stacking, or forces other than those of full covalent bonds. Recent advances in materials science and supramolecular chemistry offer building blocks for the construction of durable and selective chemical sensors. The present study was part of a project targeted at developing chemical sensors for organic cations and metal ions by exploiting the interactions between cations and anionic borate derivatives. In addition, thiophene monomers substituted with charged or neutral ion-recognition sites were constructed and investigated.

The focus of the first part of the work was to prepare anionic receptor molecules based on borate derivatives and study their complexation with *N*-heteroaromatic and tropylium cations. It was shown earlier [18] that aromatic cations like *N*-methylpyridinium, tropylium, and imidazolium form complexes with tetraphenylborate. The complexation of the cations was studied both in solution by ^1H NMR and ESIMS techniques and in solid state by X-ray crystallography. Different derivatives of aromatic borate anions synthesized within this project, some commercially available derivatives, and two neutral carriers containing aromatic anthryl groups were also studied as recognition sites for aromatic cations where *N*-methylpyridinium was the primary ion in PVC membrane-based all-solid-state ion sensors. An important part of the work was to gain further information about the nature of such complexes.

The aim of the second part of the study was to develop chemical ion sensor materials where the ion-recognition unit and the charge-compensating ion are covalently coupled to the backbone of a conductive polymer. This approach would eliminate the problem of active components leaking from the sensing membrane. The materials studied differed with respect to the receptor unit, extent of oxidation, the counteranion, and the length of the chain. The attachment of the ion-recognition and signal transduction units to the same polymer chain also allows reduction of the size of the sensor, a development of great value for the future.

Publication I reports ion-selective electrodes based on π -coordinating carriers. Derivatives of tetraphenylborate and neutral compounds containing π -coordinating anthryl groups were studied as charged and neutral carriers in PVC-based membranes. The role of the plasticizer is discussed. Publication II continues the studies of publication I and describes the synthesis of borate anions to be used as ion-recognition sites in ISEs for the detection of aromatic cations on the basis of weak noncovalent interactions. ISEs were constructed with use of poly(3,4-ethylenedioxythiophene) as solid-contact material. Paper III reports the first crystal structure of the alkali metal complex of tris[3-(2-pyridyl)pyrazolyl]-hydroborate, while paper IV focuses on 3-substituted thiophenes. The sulfonated thiophenes were used as doping ions for the construction of potentiometric ion sensors selective to silver ions.

2 Experimental

The overall goal of the study was the development of selective and sensitive potentiometric ion sensors. The first part of the experimental work involved the preparation of borate derivatives and study of their complexation and interactions with heterocyclic cations. All the complexes were characterized by NMR spectroscopy, crystal structure analysis, and/or mass spectroscopy. The synthesis of 3-substituted thiophenes and 3,4-ethylenedioxythiophene derivatives completed the study.

2.1 Reagents

The solvents were dried and distilled according to the literature procedures if needed [35]. 4-Bromodiphenylether, 4-bromobiphenyl, potassium tetrafluoroborate, potassium Tetrahydroborate, and other reagents needed for the synthesis of borate structures are described in the original papers I–III. Reagents for the preparation of sodium 2-(3-thienyloxy)ethanesulfonate and sodium 6-(3-thienyloxy)hexanesulfonate can be found in paper IV. The other reagents used in the work were obtained from Aldrich, Alfa Aesar, Ega, Eka Nobel, FF-Chemicals, Fluka, Lab-Scan, Lancaster, Merck, Riedel-de Haën, or Strem Chemicals and used without further purification. 1-Aza-15-crown-5, 1,2-oxathiane-2,2-dioxide, 2-bromoethanol, 3-bromothiophene, 3-methoxythiophene, 3-thiopheneacetic acid, 8-hydroxyquinoline, epibromohydrin, imidazole, thiodiglycolic acid, and triphenylmethyl chloride were purchased from Aldrich and used as received. Sodium ethoxide and sodium hydride (60% dispersion in mineral oil) were purchased from Aldrich and stored in a desiccator. 2-Iodoethanol, 4-(1,2,4-triazol-1-yl)phenol, 4-hydroxy-4'-nitrostilbene, *n*-butyllithium, *N,N*-dicyclohexylcarbodiimide, *p*-toluenesulfonyl chloride, and *t*-butyldimethylchlorosilane were from Alfa Aesar. Triethylamine was purchased from Fluka and distilled before use. Also 1,6-dibromohexane, 2-(2-pyridyl)ethanol, copper chromite catalyst (CuCr_2O_4), and sodium hydrogen carbonate (NaHCO_3) were from Fluka. 2-(3-Thienyl)ethanol and trimethylamine hydrochloride were from Lancaster. Pyridine was purchased from Lab-Scan and was distilled before use. Diethyl-oxalate was from Ega. Hydrochloric acid (HCl, 37%), magnesium sulfate (MgSO_4), and sodium sulfite (Na_2SO_3) were purchased from Riedel-de Haën; potassium carbonate (K_2CO_3), potassium chloride (KCl), sodium carbonate (Na_2CO_3), sodium hydrogensulfate (NaHSO_4), and sodium sulfate (Na_2SO_4) from

Merck and; acetic acid and potassium hydroxide (KOH) from FF-Chemicals. Sodium hydroxide (NaOH) was from Eka Nobel and cesium carborane from Strem Chemicals.

Analytical thin layer chromatography (TLC) was conducted on Kieselgel 60 F₂₅₄ silica gel precoated aluminium plates (Merck). Column chromatography was carried out on silica gel (Merck).

2.2 Syntheses

All borate reactions were performed in an inert atmosphere by standard Schlenk techniques. *N*-Methylpyridinium iodide, imidazolium, and 1-methylimidazolium perchlorates were prepared according to literature procedures [36,37]. Also potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate was prepared according to the literature [43,44]. Preparation of 3-[2-(toluenesulfonyl)ethyl]thiophene, the precursor for the synthesis of 3-[2-(4-oxy-4'-nitrostilbene)ethyl]thiophene, is described in the literature [53], as is the preparation of sodium 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-1-butanefulfonic acid [56] from EDOT derivatives. A general procedure for the cross-coupling reaction used in the preparation of 3-benzylthiophene likewise has been presented previously [51,52]. The monomers were synthesized for use as selective recognition sites in potentiometric ion sensors [38].

2.2.1 Preparation of borates

Six different borates (Fig. 5) were prepared for study of their properties in chemical sensors. Of these, tetrakis(4-phenylphenoxy)borate (**2**) was previously unknown, while tetrakis(4-phenoxyphenyl)borate [39] (**1**), tetrakis(biphenyl)borate [40] (**3**), tetrakis(4-phenoxy)borate [41] (**4**), and tetrakis(2-naphthyl)borate [42] (**5**) were prepared by modification of literature procedures. Potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate (**6**) was prepared according to the previously published literature procedures by attachment of aryl substituents to the C3 positions of the pyrazolyl rings [43,44]. Borate derivatives **1–5** are structurally and sterically closely related.

Lithium tetrakis(2-naphthyl)borate was originally prepared by Williams [42] in 1968 according to the general method described by Wittig and Raff [45]. A modification of the procedure was used in the preparation of sodium tetrakis(2-naphthyl)borate (**5**) and sodium tetrakis(biphenyl)borate (**3**). The synthesis of

sodium tetrakis(4-phenoxy)borate (**4**) is a modification of the procedure reported by Cole. A similar procedure was used to prepare the new compound sodium tetrakis(4-phenylphenoxy)borate (**2**). Details of the preparation, purification, and characterization of these borates can be found in the original papers I and II.

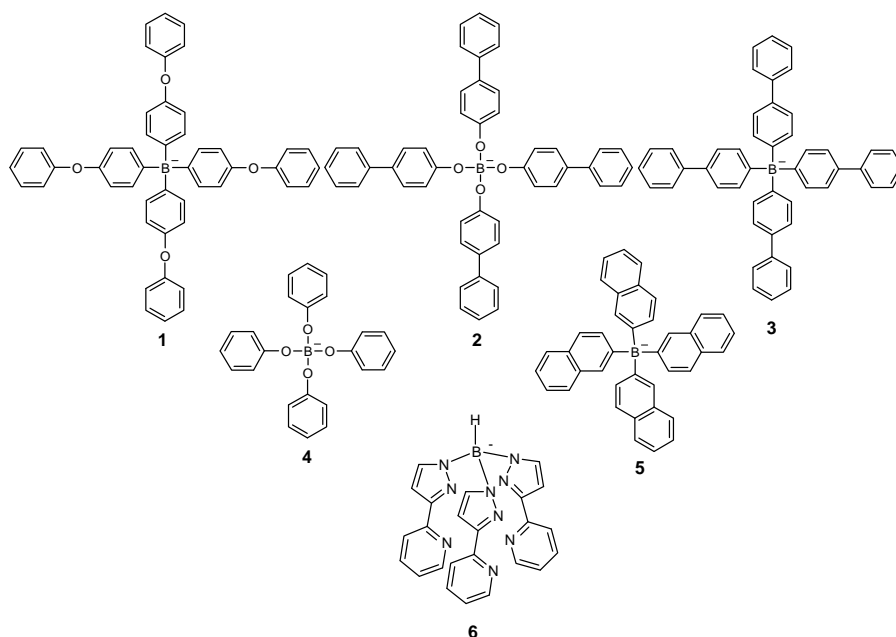


Fig. 5. Borate derivatives synthesized in this work: potassium tetrakis(4-phenoxyphenyl)borate (1), sodium tetrakis(4-phenylphenoxy)borate (2), sodium tetrakis(biphenyl)borate (3), sodium tetrakis(4-phenoxy)borate (4), sodium tetrakis(2-naphthyl)borate (5), and potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate (6).

Hydroborates containing nitrogen heterocycles have an enhanced ability to bind metal ions, offering a new dimension for complex formation. Details of the preparation, purification, and characterization of this borate can be found in the original paper [III] and references cited therein.

2.2.2 Preparation of complexes

The complexation of *N*-methylpyridinium (**7**), 1-ethyl-4-(methoxycarbonyl)pyridinium (**8**), tropylium (**9**), imidazolium (**10**), and 1-methylimidazolium (**11**) cations (Fig. 6) was studied with borate anions **1** and **3** (Fig. 5).

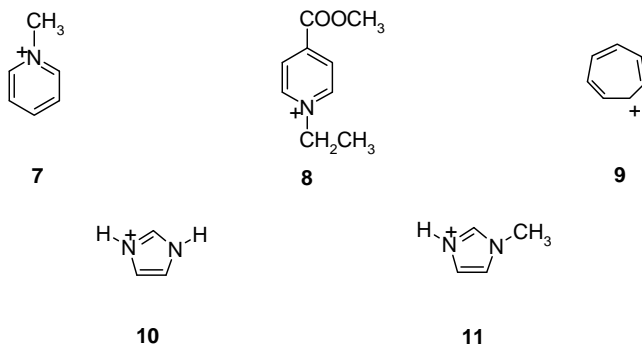


Fig. 6. Aromatic cations used in this work: *N*-methylpyridinium (-iodide), 1-ethyl-4-(methoxycarbonyl)pyridinium (-iodide), tropylium (-tetrafluoroborate), imidazolium (-perchlorate) and 1-methylimidazolium (-perchlorate).

Solid borate complexes were prepared by dissolving the salt and borate derivative separately into minimum amounts of suitable solvent and mixing the warmed solutions. The complexes precipitated soon after the mixing. Synthesis of the complexes of cations **7**, **8**, and **9** with borate anion **1** and of cation **10** with borate anion **3** is straightforward. In a suitable solvent (methanol, ethanol, or acetonitrile), the formation of a 1:1 complex was observed in all cases by NMR spectroscopy and later by X-ray crystallography. The complex formation of cations **10** and **11** with borate **1** and cations **7**, **8**, **9**, and **11** with borate **3** was detected by mass spectrometry and NMR spectroscopy, but the crystal structures of these six complexes could not be determined due to the poor quality of the crystals. Further details of the preparation, purification, and characterization of the complexes can be found in the original paper [II].

2.2.3 Preparation of 3-substituted thiophenes

Thiophenes were prepared for use as building blocks of conductive polymers with specific supramolecular properties. Conductive polymers are most often prepared by electrochemical oxidation of the corresponding monomer. The aim here was to develop potentiometric ion sensors based on conjugated polymers with covalently bound ionophores. In this approach, the molecular recognition unit and the transduction element are attached to the same molecule. Series of 3-substituted thiophene monomers and EDOT derivatives were synthesized with the aim of

incorporating them in ion-selective electrodes and studying their electrochemical properties, selectivity, and sensitivity.

The synthesis, purification, and characterization of the sulfonated thiophenes sodium 2-(3-thienyloxy)ethanesulfonate ($C_6H_7S_2O_4Na$, **12**) and sodium 6-(3-thienyloxy)hexanesulfonate ($C_{10}H_{15}S_2O_4Na$, **13**) (Fig. 7) are described in detail in paper IV. The synthesis of other, not yet published or tested monomers is reported below. All structures were purified by recrystallization or by chromatography on silica gel and characterized by NMR spectroscopy and mass spectrometry.

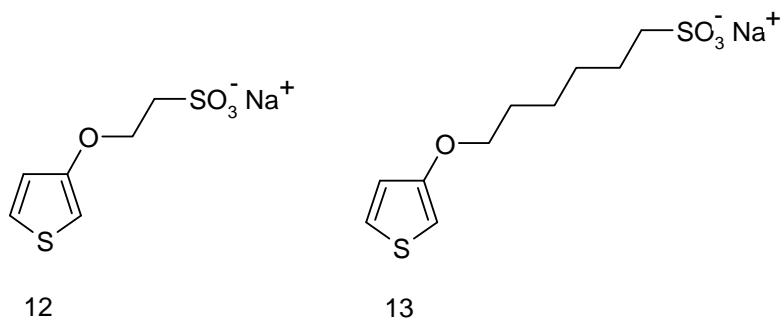


Fig. 7. Two sulfonated thiophenes synthesized in this work: sodium 2-(3-thienyloxy)ethanesulfonate (12) and sodium 6-(3-thienyloxy)hexanesulfonate (13) [IV].

Preparation of sodium 2-(3-thienyloxy)ethanesulfonate (12') from 3-(2-bromo)ethoxythiophene by a procedure [46,47] similar to that described in paper IV was carried out. 3-Methoxythiophene (4.52 g, 39.6 mmol) was dissolved with 2-bromoethanol (5.21 g, 41.7 mmol) in toluene (20 ml). $NaHSO_4$ (1.64 g) was added in one portion. After column chromatography and drying in vacuo, a pale yellow solid was obtained. 1H NMR (200 MHz, $CDCl_3$, ppm): δ 7.20 (dd, 1H, $^3J_{HH} = 5.3$ Hz, and $^4J_{HH} = 3.1$ Hz, thiophene), 6.79 (dd, 1H, $^3J_{HH} = 5.3$ Hz, and $^4J_{HH} = 1.5$ Hz, thiophene), 6.29 (dd, 1H, $^4J_{HH} = 1.6$ Hz, and $^4J_{HH} = 3.1$ Hz, thiophene), 4.28 (t, 2H, $^3J_{HH} = 6.2$ Hz, $-CH_2-$), 3.64 (t, 2H, $^3J_{HH} = 6.2$ Hz, $-CH_2-$). GC MS (EI): m/z 207 (70%) [C_6H_7OSBr], retention time 10.1 min. To a solution of Na_2SO_3 (0.73 g, 5.79 mmol) in water (12 ml) was added a solution of 3-(2-bromo)ethoxythiophene (0.78 g, 3.77 mmol) dissolved in acetone (24 ml). The mixture was refluxed and treated as described in the literature. Correct 1H NMR and mass spectra were obtained for the product.

Preparation of 2-(3-thienyloxy)ethyltriethylammonium iodide (14') [47]. Triethylamine was dried with potassium hydroxide (KOH) and distilled. The

distillate was stored over 3 Å molecular sieves. Triethylamine (0.63 g, 6.22 mmol) was added to a solution of 3-(2-iodo)ethoxythiophene (0.40 g, 1.57 mmol) dissolved in ethanol. The mixture was refluxed for 72 hours and evaporated to dryness. Recrystallization was done in diethyl ether. The product was obtained as a pale yellow solid (0.36 g, 66%). $^1\text{H NMR}$ (200 MHz, DMSO, ppm): δ 7.48 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 3.1$ Hz, thiophene), 6.81 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 1.5$ Hz, thiophene), 6.71 (dd, 1H, $^4J_{\text{HH}} = 1.5$ Hz, and $^4J_{\text{HH}} = 3.1$ Hz, thiophene), 4.35 (t, 2H, $^3J_{\text{HH}} = 4.4$ Hz, $-\text{CH}_2-\text{CH}_2-$), 3.65 (t, 2H, $^3J_{\text{HH}} = 4.7$ Hz, $-\text{CH}_2-\text{CH}_2-$), 3.35 (q, 6H, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{CH}_2-\text{CH}_3$), 1.20 (t, 9H, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{CH}_2-\text{CH}_3$). ES^+ MS: m/z 228 (100%) [$\text{C}_{12}\text{H}_{22}\text{OSN}^+$]. ES^- MS: m/z 482 (30%) [$\text{C}_{12}\text{H}_{22}\text{OSN}^+ + 2\text{I}^-$]. *Elemental analysis*: measured: C, 40.84; H, 6.49; S, 8.75; N, 3.80. $\text{C}_{12}\text{H}_{22}\text{OSNI}$ calcd: C, 40.57; H, 6.24; S, 9.02; N, 3.94 (%).

Preparation of 2-(3-thienyloxy)ethyltriethylammonium bromide (14). Triethylamine (0.64 g, 6.32 mmol) was added to a solution of 3-(2-bromo)ethoxythiophene (0.32 g, 1.55 mmol) dissolved in ethanol-THF (20 ml and 10 ml) mixture. The reaction mixture was refluxed for 48 hours and evaporated to dryness. The product was dissolved in diethyl ether and extracted with water. The water layer was collected and evaporated. $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 7.21 (dd, 1H, $^3J_{\text{HH}} = 5.2$ Hz, and $^4J_{\text{HH}} = 3.0$ Hz, thiophene), 6.71 (dd, 1H, $^3J_{\text{HH}} = 5.2$ Hz, and $^4J_{\text{HH}} = 1.5$ Hz, thiophene), 6.55 (dd, 1H, $^4J_{\text{HH}} = 1.5$ Hz, and $^4J_{\text{HH}} = 3.0$ Hz, thiophene), 4.53 (t, 2H, $^3J_{\text{HH}} = 4.6$ Hz, $-\text{CH}_2-\text{CH}_2-$), 4.16 (t, 2H, $^3J_{\text{HH}} = 4.6$ Hz, $-\text{CH}_2-\text{CH}_2-$), 3.60 (q, 6H, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{CH}_2-\text{CH}_3$), 1.42 (t, 9H, $^3J_{\text{HH}} = 7.2$ Hz, $-\text{CH}_2-\text{CH}_3$). ES^+ MS: m/z 228 (100%) [$\text{C}_{12}\text{H}_{22}\text{OSN}^+$]. *Exact mass*: 228.1446 (M^+) (calcd. for $\text{C}_{12}\text{H}_{22}\text{NOS}$, 228.1422).

Preparation of 2-(3-thienyloxy)ethylpyridinium iodide (15'). Dried pyridine (2 ml, $d = 0.978$ g/ml, 24.7 mmol) was added to a solution of 3-(2-iodo)ethoxythiophene (0.57 g, 2.24 mmol) dissolved in THF (20 ml). The mixture was refluxed for 48 hours and evaporated to dryness. Recrystallization was done in diethyl ether. The product was obtained as a pale yellow solid (0.51 g, 68%). $^1\text{H NMR}$ (200 MHz, CD_3CN , ppm): δ 8.81 (d, 2H, $^3J_{\text{HH}} = 5.3$ Hz, pyridinium), 8.54 (t, 1H, $^3J_{\text{HH}} = 7.9$ Hz, pyridinium), 8.05 (t, 2H, $^3J_{\text{HH}} = 7.1$ Hz, pyridinium), 7.28 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 3.1$ Hz, thiophene), 6.73 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 1.7$ Hz, thiophene), 6.47 (dd, 1H, $^4J_{\text{HH}} = 1.6$ Hz, and $^4J_{\text{HH}} = 3.2$ Hz, thiophene), 4.92 (t, 2H, $^3J_{\text{HH}} = 4.8$ Hz, $-\text{CH}_2-$), 4.45 (t, 2H, $^3J_{\text{HH}} = 4.8$ Hz, $-\text{CH}_2-$). ES^+ MS: m/z 206 (100%) [$\text{C}_{11}\text{H}_{12}\text{SON}^+$]. ES^- MS: m/z 460 (25%) [$\text{C}_{11}\text{H}_{12}\text{SON}^+ + 2\text{I}^-$]. *Elemental analysis*: measured: C, 39.36; H, 3.32; S, 9.44; N, 4.29. $\text{C}_{11}\text{H}_{12}\text{SONI}$ calcd: C, 39.65; H, 3.63; S, 9.62; N, 4.20 (%).

Preparation of 2-(3-thienyloxy)ethylpyridinium bromide (15). Pyridine (0.49 g, 6.19 mmol) was added to a solution of 3-(2-bromo)ethoxythiophene (0.32 g, 1.55 mmol) dissolved in ethanol (20 ml). The reaction mixture was refluxed for 72 hours and evaporated to dryness. The mixture was dissolved in diethyl ether and extracted with water. The water layer was collected and evaporated to dryness. $^1\text{H NMR}$ (200 MHz, D_2O , ppm): δ 8.92 (d, 2H, $^3J_{\text{HH}} = 5.5$ Hz, pyridinium), 8.60 (t, 1H, $^3J_{\text{HH}} = 7.9$ Hz, pyridinium), 8.10 (t, 2H, $^3J_{\text{HH}} = 7.1$ Hz, pyridinium), 7.34 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 3.2$ Hz, thiophene), 6.79 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 1.6$ Hz, thiophene), 6.57 (dd, 1H, $^4J_{\text{HH}} = 1.6$ Hz, and $^4J_{\text{HH}} = 3.2$ Hz thiophene), 5.03 (t, 2H, $^3J_{\text{HH}} = 4.8$ Hz, $-\text{CH}_2-$), 4.58 (t, 2H, $^3J_{\text{HH}} = 4.8$ Hz, $-\text{CH}_2-$). $\text{ES}^+ \text{MS}$: m/z 206 (100%) [$\text{C}_{11}\text{H}_{12}\text{SON}^+$]. *Exact mass*: 206.0652 (M^+) (calcd. for $\text{C}_{11}\text{H}_{12}\text{NOS}$, 206.0640).

Preparation of 3-(acetyl monoaza 15-crown-5)thiophene (16) [48,49]. In a 100-ml round-bottom flask fitted with a thermometer and a magnetic stirrer, 3-thiopheneacetic acid (0.20 g, 1.41 mmol) dissolved in CH_2Cl_2 (5 ml) was added to a solution of 1-aza-15-crown-5 (0.40 g, 1.82 mmol) dissolved in a solution of CH_2Cl_2 (10 ml) and triethylamine (ca. 0.5 ml). The mixture was cooled with an ice-bath. N,N' -Dicyclohexylcarbodiimide (0.36 g, 1.74 mmol) was added and the obtained mixture was allowed to warm up to room temperature and maintained under stirring for 24 h. Acetic acid (0.3 ml) was added to destroy the DCC excess. After one hour the precipitated N,N' -dicyclohexylurea was filtered and washed with a small amount of dichloromethane. The combined organic layers were washed with water, dried (MgSO_4), and concentrated under reduced pressure. The obtained crude product was purified by chromatography on a silica column eluted with n-heptane/ethyl acetate (30:70) solution. $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 7.31 (dd, 1H, $^3J_{\text{HH}} = 4.9$ Hz, and $^4J_{\text{HH}} = 3.0$ Hz, thiophene), 7.12 (dd, 1H, $^4J_{\text{HH}} = 1.3$ Hz, and $^4J_{\text{HH}} = 2.9$ Hz, thiophene), 7.03 (dd, 1H, $^3J_{\text{HH}} = 5.0$ Hz, and $^4J_{\text{HH}} = 1.4$ Hz, thiophene), 3.80–3.55 (m, 20H, crown), 2.13 (s, 2H, $-\text{CH}_2-$). $\text{ES}^+ \text{MS}$: m/z 366 (100%) [$\text{C}_{16}\text{H}_{25}\text{SO}_5\text{N}+\text{Na}^+$]. *Exact mass*: 366.1346 (M^+) (calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_5\text{NaS}$, 366.1351).

Preparation of 3-[2-((triphenylmethyl)oxy)ethoxy]thiophene (17) [50]. Triphenylmethyl chloride (2.98 g, 10.7 mmol) was added to a solution of 3-(hydroxyethoxy)thiophene (1.03 g, 7.14 mmol) dissolved in pyridine (8 ml). The solution was refluxed for 24 hours under an atmosphere of nitrogen, after which 10 ml of distilled ice water was poured into the reaction vessel. The crude product was dissolved in diethyl ether and separated from the aqueous phase, and the water layer was extracted with diethyl ether (3×30 ml). The organic layer was

washed with 1 M hydrochloric acid (10 ml), saturated sodium hydrogen carbonate solution (NaHCO_3), and water. The ether extract was dried over magnesium sulfate overnight, filtered, and concentrated in vacuo. 3-[2-((Triphenylmethyl)-oxy)ethoxy]thiophene was purified by silica gel chromatography, with ethyl acetate and hexane (10:90) solution used as the eluent. The product crystallized as colorless crystals (0.77 g, 38%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 7.51–7.22 (m, 15H, phenyls), 7.18 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 3.2$ Hz, thiophene), 6.80 (dd, 1H, $^3J_{\text{HH}} = 5.3$ Hz, and $^4J_{\text{HH}} = 1.5$ Hz, thiophene), 6.23 (dd, 1H, $^4J_{\text{HH}} = 1.5$ Hz, and $^4J_{\text{HH}} = 3.2$ Hz, thiophene), 4.11 (t, 2H, $^3J_{\text{HH}} = 5.1$ Hz, $-\text{CH}_2-$), 3.42 (t, 2H, $^3J_{\text{HH}} = 5.1$ Hz, $-\text{CH}_2-$). ES^+MS : m/z 409 (100%) [$\text{C}_{25}\text{H}_{22}\text{O}_2\text{S}+\text{Na}^+$]. EI^+MS : m/z 386 [$\text{C}_{25}\text{H}_{22}\text{O}_2\text{S}$]. *Elemental analysis*: measured: C, 78.50; H, 5.75; S, 8.20. $\text{C}_{25}\text{H}_{22}\text{O}_2\text{S}$ calcd: C, 77.69; H, 5.74; S, 8.29 (%).

Preparation of 3-benzylthiophene (18) [51,52]. A solution of benzylchloride 2.27 g (17.9 mmol) in diethyl ether (40 ml) was added to oven-dried magnesium turnings 2.78 g (114.4 mmol) containing an iodine crystal via a double-ended needle. The mixture was stirred under nitrogen and warmed until the reaction commenced. The suspension was stirred for 20 more minutes with occasional warming. 3-Bromothiophene (2.03 g, 12.5 mmol) and [1,3-bis-(diphenylphosphine)propane]nickel(II)chloride (ca. 2 mg) were dissolved under nitrogen in diethyl ether (30 ml), and the mixture was cooled in an ice-bath. Grignard reagent was added to the suspension of 3-bromothiophene and nickel-phosphine catalyst via a double-ended needle over a period of 30 minutes. The mixture was allowed to react overnight and treated with 1 M HCl and water. The organic layers were dried over Na_2SO_4 , filtered, and evaporated under reduced pressure. The product was purified further by distillation. Yield 0.64 g (29%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 7.33–7.13 (m, phenyl and thiophene), 6.88 (m, thiophene), 3.95 (s, $-\text{CH}_2-$).

Preparation of 3-[2-(toluenesulfonyl)ethyl]thiophene (19) [53]. Tosyl chloride (6.01 g, 31.5 mmol) was added for 20 minutes to a solution of 2-(3-thienyl)ethanol (2.01 g, 15.7 mmol) in dry pyridine (24 ml), cooled in an ice-bath. The reaction mixture was stirred at room temperature for 40 minutes, stored overnight in a refrigerator, and then poured under stirring into 200 g of ice and water. The white crystalline product was filtered, washed with distilled water, and dried in vacuo at room temperature (yield 3.74 g, 85%). Satisfactory analytical data were obtained [53].

Preparation of 3-[2-(4-oxy-4'-nitrostilbene)ethyl]thiophene (20) [53]. A stirred mixture of 4-hydroxy-4'-nitrostilbene (0.30 g, 1.24 mmol), 3-[2-(toluene-

sulfonyl)ethyl]thiophene (0.38 g, 1.35 mmol), and finely powdered K_2CO_3 (0.61 g) in dry *N,N*-DMF (6 ml) was heated at 100 °C for 24 hours. After cooling to room temperature, the reaction mixture was poured under stirring into 1 M HCl (30 ml) and filtered. The residue was washed with distilled water to neutrality and recrystallized from isopropanol to give a yellow crystalline solid (yield 0.41 g, 86%). Satisfactory analytical data were obtained [53].

Preparation of 3-[2-(4-oxy-1,2,4-triazol-1-yl)ethyl]thiophene (21). This compound was synthesized following the procedure described for the preparation of derivative 3-[2-(4-oxy-4'-nitrostilbene)ethyl]thiophene (**20**) but using 4-(1,2,4-triazol-1-yl)phenol (0.39 g, 2.42 mmol) and 3-[2-(toluenesulfonyl)ethyl]thiophene (0.71 g, 2.51 mmol). After refluxing, the mixture was washed with distilled water, extracted with chloroform (4×20 ml), and concentrated under reduced pressure (yield 0.44 g, 67%). 1H NMR (200 MHz, CD_3OH , ppm): δ 8.95 (s, 1H, triazolyl), 8.13 (s, 1H, triazolyl), 7.69 (d, 2H, $^3J_{HH} = 9.0$ Hz, phenyl), 7.34 (dd, 1H, $^3J_{HH} = 4.8$ Hz, and $^4J_{HH} = 3.0$ Hz, thiophene), 7.20 (m, 1H, thiophene), 7.11–7.07 (m, 1H thiophene, and 2H phenyl), 4.25 (t, 2H, $^3J_{HH} = 6.7$ Hz, $-CH_2-$), 3.13 (t, 2H, $^3J_{HH} = 6.7$ Hz, $-CH_2-$). ES^+MS : m/z 272 (100%) [$C_{14}H_{13}OSN_3+H$] $^+$. *Elemental analysis*: measured: C, 62.17; H, 4.76; S, 11.85; N, 15.39. $C_{14}H_{13}OSN_3$ calcd: C, 61.97; H, 4.83; S, 11.82; N, 15.49 (%). *Exact mass*: 272.0865 (M+H) $^+$ (calcd. for $C_{14}H_{14}N_3OS$, 272.0858).

Preparation of 3-[2-(8-oxy-2-methylquinoline)ethyl]thiophene (22). Compound **22** was synthesized following the procedure described for the preparation of derivative **20** by using 8-hydroxyquinaldine (0.50 g, 3.14 mmol) and 3-[2-(toluenesulfonyl)ethyl]thiophene (0.94 g, 3.33 mmol). After refluxing for 24 hours, the mixture was poured into water, extracted with chloroform, and purified further by silica gel chromatography with a mixture of ethyl acetate/hexane (10:90) as the eluent. 1H NMR (500 MHz, CD_3OD , ppm): δ 6.80 (d, 1H, $^3J_{HH} = 8.4$ Hz, quinaldine), 6.12–6.06 (m, 4H, quinaldine), 5.98 (m, 1H, thiophene), 5.87 (m, 1H, thiophene), 5.81 (m, 1H, thiophene), 3.09 (t, 2H, $^3J_{HH} = 7.1$ Hz, $-CH_2-$), 2.03 (t, 2H, $^3J_{HH} = 7.0$ Hz, $-CH_2-$), 1.47 (s, $-CH_3$, 3H). $^{13}C\{^1H\}$ NMR (500 MHz, CD_3OD , ppm): δ 157.20, 152.58, 138.10, 137.51, 136.27, 128.07, 128.04, 124.86, 124.26, 121.15, 120.86, 118.93, 107.71, 67.91, 28.47, 22.85. ES^+MS : m/z 270 (100%) [$C_{16}H_{15}OSN+H$] $^+$. *Exact mass*: 270.0941 (M+H) $^+$ (calcd. for $C_{16}H_{16}NOS$, 270.0953).

Preparation of 3-[2-(2-pyridine-ethoxy)ethyl]thiophene (23). Compound **23** was synthesized from sodium 2-(2-pyridyl)ethoxide and 3-[2-(toluenesulfonyl)ethyl]thiophene. Sodium hydride (0.38 g as an oil dispersion, 9.50

mmol) was weighed into a three-necked flask. With the aid of a double-ended needle, the mineral oil was removed with THF. To the pure NaH, kept in an ice-bath, was added 15 ml of freshly distilled THF. A total of 0.52 g (4.22 mmol) of 2-(2-pyridyl)ethanol was added to the NaH suspension in THF (10 ml) via a double-ended needle while the mixture was stirred. After completion of the addition, the reaction mixture was stirred one more hour in an ice-bath, during which time the reaction mixture turned pale orange. 3-[2-(Toluenesulfonyl)-ethyl]thiophene (1.29 g, 4.57 mmol) and K_2CO_3 (1.96 g) were dissolved in THF (15 ml) and added at room temperature to the reaction mixture and stirred for one hour. After refluxing overnight, the mixture was cooled, poured into water, and extracted with diethyl ether (3×30 ml). The product was further purified by silica gel chromatography, using first a mixture of ethyl acetate/hexane (10:90) as the eluent and then chloroform. 1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.52 (d, 1H, $^3J_{HH} = 4.4$ Hz, pyridine), 7.59 (t, 1H, $^3J_{HH} = 7.6$ Hz, pyridine), 7.30–6.90 (m, 2H pyridine, 3H thiophene), 3.87–3.80 (m, 2H, pyridine- CH_2-CH_2-), 3.66 (t, 2H, $^3J_{HH} = 6.8$ Hz, thiophene- CH_2-CH_2-), 3.06 (t, 2H, $^3J_{HH} = 6.6$ Hz, pyridine- CH_2-CH_2-), 2.84–2.94 (m, 2H, thiophene- CH_2-CH_2-). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, ppm): δ 159.20, 149.25, 139.33, 136.64, 128.64, 125.29, 123.95, 121.60, 121.26, 71.15, 70.25, 38.64, 30.65. ES^+MS : m/z 234 (100%) [$C_{13}H_{15}OSN+H$] $^+$. *Exact mass*: 234.0956 (M+H) $^+$ (calcd. for $C_{13}H_{16}NOS$, 234.0953).

2.2.4 Preparation of 3,4-ethylenedioxythiophene derivatives

The electropolymerization of precursors derivatized with covalently attached functional groups represents the most straightforward method for the synthesis of functional, conjugated polymers [54]. Both 3,4-ethylenedioxythiophene (EDOT) and PEDOT have lower oxidation potentials than 3-substituted thiophenes. In the oxidized form, poly(3,4-ethylenedioxythiophene) (PEDOT) also exhibits higher stability than other polythiophenes under both ambient and elevated temperature conditions [55].

Preparation of 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-ylmethanol (i.e., hydroxymethyl-EDOT) followed the literature procedure [56,57]. All the derivatives described below were solids, which simplified their purification by recrystallization or column chromatography.

Preparation of sodium 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid (24) [57]. Hydroxymethyl-EDOT (0.50 g, 2.90 mmol) dissolved in toluene (20 ml) was added to a NaH suspension (0.14 g as an

oil dispersion, 3.5 mmol) under a nitrogen atmosphere via a double-ended needle. The resulting mixture was refluxed for one hour, after which 1,4-butanedisulfone (i.e., 1,2-oxathiane-2,2-dioxide) (0.41 g, 3.01 mmol) dissolved in THF (8 ml) was slowly added. The mixture was stirred for two more hours and then allowed to cool. Acetone (45 ml) was poured into the mixture under vigorous stirring. The suspension was filtered, washed with hot acetone, and concentrated at 100 °C under vacuum. The total yield of the pale orange powder was 0.26 g (27%). ¹H NMR (200 MHz, D₂O, ppm): δ 6.55 (s, 2H, -C=CH-S-), 4.51–4.43 (m, 1H, -CH₂-CH-CH₂-), 4.34 (dd, 1H, ²J_{HH} = 12.0 Hz, and ³J_{HH} = 2.3 Hz, -O-CH₂-CH-), 4.15 (dd, 1H, ²J_{HH} = 11.9 Hz, and ³J_{HH} = 6.8 Hz, -O-CH₂-CH), 3.81–3.78 (m, 2H, -CH₂-), 3.65 (t, 2H, ³J_{HH} = 6.0 Hz, -CH₂-), 2.97 (t, 2H, ³J_{HH} = 7.5 Hz, -CH₂-), 1.86–1.72 (m, 4H, -O-CH₂-CH₂-CH₂-CH₂-). *ES*⁺ *MS*: m/z 353 (100%) [C₁₁H₁₅O₆S₂⁻+2Na⁺]. *ES*⁻ *MS*: m/z 307 (100%) [C₁₁H₁₅O₆S₂⁻]. *Exact mass*: 307.0314 (M)⁻ (calcd. for C₁₁H₁₅O₆S₂, 307.0310).

Preparation of 2-[(6-bromohexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin [58]. Sodium hydride (0.40 g as an oil dispersion, 10.0 mmol) dissolved in freshly distilled THF (16 ml) was placed in an ice-bath. Hydroxymethyl-EDOT (1.14 g, 6.62 mmol) dissolved in THF (20 ml) was added to the NaH suspension via a double-ended needle. The mixture was stirred for one hour at 0 °C, after which 1,6-dibromohexane (4.16 g, 17.1 mmol) dissolved in THF (16 ml) was added. The mixture was left to warm to room temperature (1 hour) and refluxed overnight. The reaction mixture was then poured into distilled water (150 ml) and extracted with diethyl ether (3×150 ml). The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo. The compound was purified by silica gel chromatography, with a mixture of ethyl acetate/hexane (20:80) used as the eluent. The total yield of the pale yellow powder was 1.06 g (48%). ¹H NMR (200 MHz, CDCl₃, ppm): δ 6.33 (s, 2H, -C=CH-S-), 4.35–4.21 (m, 1H, -O-CH₂-CH- and 1H, -CH₂-CH-CH₂-), 4.05 (dd, 1H, ²J_{HH} = 11.6 Hz, and ³J_{HH} = 7.5 Hz, -O-CH₂-CH-), 3.73–3.38 (m, 2H, -CH-CH₂-O-CH₂-; 2H, -CH-CH₂-O-CH₂-CH₂- and 2H, -CH₂-Br), 1.93–1.79 (m, 2H, -CH₂-), 1.67–1.54 (m, 2H, -CH₂-), 1.50–1.32 (m, 4H, -CH₂-CH₂-CH₂-CH₂-Br). *GC MS (EI)*: m/z 334 (56%) [C₁₃H₁₉O₃SBr], m/z 255 (100%) [C₁₃H₁₉O₃S⁺]; retention time 18.0 min.

Preparation of 6-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-hexylpyridinium bromide (25). Freshly distilled pyridine (0.49 g, 6.19 mmol) was added to a solution of 2-[(6-bromohexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin (0.17 g, 0.51 mmol) dissolved in THF (18 ml). The reaction

mixture was refluxed for 72 hours under a nitrogen atmosphere and evaporated to dryness. The product was recrystallized from diethyl ether. The total yield of the off-white powder was 0.16 g (77%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 9.47 (d, 2H, $^3J_{\text{HH}} = 5.5$ Hz, pyridinium $-\text{CH}=\text{N}-\text{CH}=\text{}$), 8.47 (t, 1H, $^3J_{\text{HH}} = 7.8$ Hz, pyridinium $-\text{CH}=\text{CH}-\text{CH}=\text{}$), 8.09 (t, 2H, $^3J_{\text{HH}} = 7.0$ Hz, pyridinium $-\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{}$), 6.33 (s, 2H, thiophene $-\text{C}=\text{CH}-\text{S}-$), 5.0 (t, 2H, $^3J_{\text{HH}} = 7.5$ Hz, $-\text{CH}_2-\text{CH}_2-\text{N}-$), 4.33–3.99 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}-$ and 1H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 3.64 (t, 2H, $^3J_{\text{HH}} = 5.4$ Hz, $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-$), 3.48 (t, 2H, $^3J_{\text{HH}} = 6.0$ Hz, $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$), 2.15–2.0 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}-$), 1.50–1.38 (m, 6H, $-\text{O}-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2-$). ES^+MS : m/z 334 (100%) [$\text{C}_{18}\text{H}_{24}\text{O}_3\text{SN}^+$]. ES^-MS : m/z 494 (100%) [$\text{C}_{18}\text{H}_{24}\text{O}_3\text{SN}^+ + 2\text{Br}^-$]. *Exact mass*: 334.1487 (M^+) (calcd. for $\text{C}_{18}\text{H}_{24}\text{NO}_3\text{S}$, 334.1477).

Preparation of 6-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-hexyltriethylammonium bromide (26). Triethylamine (0.54 g, 5.33 mmol) was added to a solution of 2-[(6-bromohexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin (0.45 g, 1.34 mmol) dissolved in ethanol (25 ml). The reaction mixture was refluxed for 72 hours under a nitrogen atmosphere and evaporated to dryness. The product was recrystallized from diethyl ether. The total yield of the pale yellow powder was 0.28 g (47%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 6.33 (s, 2H, $-\text{C}=\text{CH}-\text{S}-$), 4.33–4.01 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}-$ and 1H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 3.73–3.46 (m, 2H, $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-$ and 2H, $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.36–3.08 (m, 6H, $-\text{N}-\text{CH}_2-\text{CH}_3$), 1.75–1.57 (m, 8H, $-\text{O}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-$), 1.49–1.36 (m, 9H, $-\text{N}-\text{CH}_2-\text{CH}_3$). ES^+MS : m/z 356 (100%) [$\text{C}_{19}\text{H}_{34}\text{O}_3\text{SN}^+$]. *Exact mass*: 356.2263 (M^+) (calcd. for $\text{C}_{19}\text{H}_{34}\text{NO}_3\text{S}$, 356.2259).

Preparation of 2-[(6-hydroxyhexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin. The preparation of 2-[(6-triphenylmethyl)oxyhexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin required the synthesis of 2-[(6-hydroxyhexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin as a precursor. A solution of 2-[(6-bromohexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin (0.89 g, 2.65 mmol) dissolved in 16% NaOH (20 ml) and dioxane (8 ml) was refluxed under vigorous stirring overnight. The reaction was carried out under a nitrogen atmosphere. The mixture was extracted with diethyl ether (3×20 ml). The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo. A pale yellow oil was obtained. $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 6.33 (s, 2H, $-\text{C}=\text{CH}-\text{S}-$), 4.35–4.19 (m, 1H, $-\text{O}-\text{CH}_2-\text{CH}-$ and 1H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 4.05 (dd, 1H, $^2J_{\text{HH}} = 11.6$ Hz, and $^3J_{\text{HH}} = 7.6$ Hz, $-\text{O}-\text{CH}_2-\text{CH}-$), 3.73–3.38 (m, 2H, $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-$; 2H $-\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ and 2H, $-\text{CH}_2-\text{OH}$), 1.93–1.35 (m, 8H,

-O-CH₂-(CH₂)₄-CH₂- and 1H, -OH). GC MS (EI): m/z 272 (100%) [C₁₃H₂₀O₄S], retention time 17.1 min.

Preparation of 2-[(6-triphenylmethyl)oxyhexyl]oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin (27). Triphenylmethyl chloride (0.89 g, 3.19 mmol) was added to a solution of 2-[(6-hydroxyhexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin (0.58 g, 2.13 mmol) dissolved in pyridine (10 ml). The solution was refluxed for 24 hours under a nitrogen atmosphere, after which 15 ml of distilled ice water was poured into the reaction vessel. The crude yellow product was extracted with diethyl ether (3×30 ml). The organic layer was washed with 1 M hydrochloric acid (15 ml), saturated sodium hydrogen carbonate solution (NaHCO₃), and distilled water. The ether extract was dried over magnesium sulfate overnight, filtered, and concentrated in vacuo. The monomer was purified by silica gel chromatography, using ethyl acetate and hexane (10:90) solution as the eluent. The product was crystallized as white crystals (0.59 g, yield 54%). ¹H NMR (200 MHz, CDCl₃, ppm): δ 7.34–7.23 (m, 15H, phenyls), 6.32 (s, 2H, -C=CH-S-), 4.36–4.18 (m, 1H, -O-CH₂-CH- and 1H, -CH₂-CH-CH₂-), 4.03 (dd, 1H, ²J_{HH} = 11.6 Hz, and ³J_{HH} = 7.5 Hz, -O-CH₂-CH), 3.73–3.58 (m, 2H, -CH-CH₂-O-CH₂- and 2H, -CH-CH₂-O-CH₂-CH₂-), 3.53–3.43 (m, 2H, -CH₂-), 3.04 (t, 2H, ³J_{HH} = 6.6 Hz, -CH₂-CH₂-O-CPh₃), 1.47–0.83 (m, 8H, -O-CH₂-(CH₂)₄-CH₂-). ES⁺MS: m/z 537 (100%) [C₃₂H₃₄O₄S+Na⁺]. Exact mass: 537.2067 (M)⁺ (calcd. for C₃₂H₃₄O₄NaS, 537.2076).

2.2.5 Preparation of thiophene 3-substituted by carborane

A C-derivative of the *closo*-dodecacarborane anion (CB₁₁H₁₂⁻) with a polymerizable group for use in ion-selective electrodes was synthesized. The synthesis of [Me₃NH][HO(CH₂)₂-CB₁₁H₁₁], the precursor for product **28**, was according to the literature [96].

Preparation of trimethylammonium 3-[(carborane-ethoxy)ethyl]-thiophene (28). Tosyl chloride (1.84 g, 9.65 mmol) was slowly added to a solution of [Me₃NH][HO(CH₂)₂-CB₁₁H₁₁] (ca. 1 g) in dry pyridine (8 ml), cooled in an ice-bath. The reaction mixture was stirred at room temperature for 1 hour and stored overnight in a refrigerator. It was then poured under stirring into 100 g of ice and water. The off-white product was filtered, washed with distilled water, and dried in vacuo. The product was purified by silica gel chromatography, with a mixture of CH₂Cl₂/acetonitrile (80:20) as the eluent, and characterized by mass spectroscopy. ES⁻MS: m/z 341 (80%) [CH₃-C₆H₄-SO₂-O-CB₁₁H₁₁⁻]. The title

product was synthesized from sodium 2-thienylethoxide and the tosyl derivative of the carborane described above. Sodium hydride (0.15 g as an oil dispersion, 3.75 mmol) was weighed into a round-bottom flask with side arms and dissolved in 12 ml of freshly distilled THF. Sodium hydride was kept in an ice-bath. A total of 0.16 g (1.25 mmol) of 2-thienylethanol dissolved in THF (8 ml) was added to the NaH suspension via a double-ended needle while the mixture was stirred. After completion of the addition, the reaction mixture was stirred for one more hour in an ice-bath. The tosyl derivative of the carborane [$\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_2\text{-O-CB}_{11}\text{H}_{11}$] (0.16 g, 0.47 mmol), and K_2CO_3 (0.23 g) were dissolved in THF (10 ml) and added at room temperature to the reaction mixture and stirred for one hour after. The mixture was then refluxed overnight, cooled, poured into water (40 ml), and extracted with diethyl ether (3×30 ml). The product was further purified by chromatography on silica gel, with a mixture of CH_2Cl_2 /acetonitrile (80:20) as the eluent. The presence of impurities caused uncertainty in the interpretation of the NMR data. Moreover, the quantity of sample available was not sufficient for further purification. $^1\text{H NMR}$ (200 MHz, CDCl_3 , ppm): δ 7.32–7.20 and 7.10–6.94 (m, thiophene), 3.92–3.78, 3.70–3.58, 3.25–3.15 and 2.95–2.83 (m, $-\text{CH}_2-$), 2.20–0.40 (m, carborane). *ES⁻ MS*: m/z 297 (100%) [$\text{C}_8\text{H}_{11}\text{OS-CB}_{11}\text{H}_{11}$] $^-$. *Exact mass*: 298.2371 (M^-) (calcd. for $\text{C}_9\text{H}_{21}\text{B}_{11}\text{OS}$, 298.2337).

2.3 Instrumentation and methods

NMR spectroscopy: The borates were characterized by ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectroscopy. Although X-ray crystallography is the most accurate source of structural information on borates, NMR is important, especially in elucidating the course of substitution reactions. Natural boron consists of two stable naturally occurring isotopes: ^{10}B (19.6%) and ^{11}B (80.4%). Most often ^{11}B NMR is used for the characterization of borates. Here, the complexes were characterized by ^1H NMR and the thiophene derivatives mainly by ^1H NMR. If assistance in the interpretation was needed, $^{13}\text{C}\{-^1\text{H}\}$, DEPT, or two-dimensional H,C-correlated HMBC was applied as well. Most of the ^1H NMR spectra were measured on a Bruker DPX200 NMR spectrometer, some on a Bruker DRX500 NMR spectrometer. The ^{11}B NMR spectra were recorded on the Bruker DPX200 spectrometer, reported against external $\text{BF}_3 \cdot \text{OEt}_2$, and $^{13}\text{C}\{-^1\text{H}\}$, DEPT, and 2D HMBC NMR spectra were measured on the Bruker DRX500. Tetramethylsilane

(TMS) was used as an internal standard in organic solvents. All measurements except stability constant measurements were carried out at room temperature.

^1H NMR is a useful technique for the investigation of rapid reversible complexation. When host (H) and guest (G) interact in solution forming 1:1 complexes (C) according to equation 1, the stability constant K in the equilibrium can be expressed by equation 2, where $[\text{H}]_0$ and $[\text{G}]_0$ are the initial analytical concentrations of host and guest and $[\text{C}]$ is the concentration of the complex at equilibrium.



$$K = \frac{[\text{C}]}{([\text{H}]_0 - [\text{C}])([\text{G}]_0 - [\text{C}])} \quad (2)$$

When the host–guest system involves fast exchange of the C and G in NMR scale and the observed nucleus is on the guest, the observed chemical shift is the weighted average of the shifts of the protons in the complexed form, δ_{C} , and in the uncomplexed species, δ_{G} . If the solvent effect is ignored and the behavior of all the species in diluted solution is assumed to be ideal, the stability constant K can be calculated according to the Rose-Drago equation (3) or the Benesi-Hildebrand equation (4), where $\Delta\delta_{\text{obs}} = \delta_{\text{obs}} - \delta_{\text{G}}$ [59,60,61,62]. The Rose-Drago equation contains two variables, $[\text{C}]$ and δ_{C} , which can be calculated. If at least 10-fold excess of host is used, i.e. $[\text{H}]_0 \gg [\text{G}]_0$, equation 3 reduces to the Benesi-Hildebrand equation 4.

$$\frac{[\text{H}]_0}{\Delta\delta_{\text{obs}}} = \frac{1}{\delta_{\text{C}} - \delta_{\text{G}}} \cdot ([\text{H}]_0 + [\text{G}]_0 - [\text{C}]) + \frac{1}{K(\delta_{\text{C}} - \delta_{\text{G}})} \quad (3)$$

$$\frac{1}{\Delta\delta_{\text{obs}}} = \frac{1}{K(\delta_{\text{C}} - \delta_{\text{G}})} \cdot \frac{1}{[\text{H}]_0} + \frac{1}{\delta_{\text{C}} - \delta_{\text{G}}} \quad (4)$$

The stability constants were measured using an excess of host and were calculated by the Benesi-Hildebrand equation (4).

Mass spectroscopy: Accurate masses were recorded with a Micromass LCT spectrometer using ESI+ or ESI- methods and a TOF mass analyzer. GC analysis was completed on a Micromass Quattro II (column OV-1701, 30 m \times 0.32 mm). The mass spectrometer was operated in electron ionization (EI) mode, with electron energy of 70 eV.

X-Ray crystallography: Suitable single crystals were obtained by slow evaporation of the solvent. X-Ray measurements were performed at the

University of Jyväskylä with a Nonius Kappa CCD diffractometer. Graphite monochromated MoK α radiation [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$] and temperature of $173.0 \pm 0.1 \text{ K}$ were used in all cases. In addition, *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate was measured at $263.0 \pm 0.1 \text{ K}$ owing to the decay of the crystals at low temperatures. Further details of the measurements can be found in the original papers II and III.

Ion-selective electrodes: Electrochemical measurements were performed at Åbo Akademi University. Plasticized polymer membrane-based ion-selective electrodes (ISEs) were prepared by using poly(3,4-ethylenedioxythiophene) (PEDOT) as solid contact material. PEDOT was deposited on a glassy carbon disk electrode (area = 0.07 cm^2) by galvanostatic electrochemical polymerization (current = 0.014 mA , time = 714 s) from a deaerated aqueous solution containing 0.01 M 3,4-ethylenedioxythiophene and 0.1 M sodium poly(4-styrenesulfonate), NaPSS. The electropolymerization was accomplished with an Autolab General Purpose Electrochemical System (Eco Chemie B.V., The Netherlands) connected to a conventional one-compartment three-electrode electrochemical cell. The glassy carbon disk electrode was used as a working electrode, a glassy carbon rod as an auxiliary electrode, and a Ag/AgCl (3 M KCl) as a reference electrode. Before polymerization, the glassy carbon disk electrode was polished with $0.3 \text{ }\mu\text{m}$ alumina, rinsed with deionized water, and cleaned ultrasonically. After electropolymerization, the glassy carbon/PEDOT electrodes were rinsed with deionized water and conditioned for at least 24 h in 0.01 M *N*-methylpyridinium iodide solution. The electrodes were then coated with ion-selective membranes of the following composition in % (w/w): tetraarylborate 1.0–2.2%, PVC 32–33%, and *o*-NPOE 65–66%. The membrane ingredients were dissolved in THF and applied to the electrodes with a micropipette. After evaporation of THF the ion-selective membrane covered the underlying PEDOT film completely. The resulting ISEs were conditioned in 0.01 M *N*-methylpyridinium iodide for at least 24 h . Potentiometric measurements were performed with a homemade multichannel mV meter with Ag/AgCl (3 M KCl) as reference electrode. The measurements were conducted at room temperature ($23 \pm 2 \text{ }^\circ\text{C}$). Further details of the measurements can be found in the original papers I, II, and IV.

Elemental analyses: Elemental analyses were carried out on a Perkin Elmer 2400 Series II CHNS/O analyzer.

3 Results and discussion

The purpose of the first part of the study was to synthesize various borate derivatives and explore their complexation with aromatic nitrogen heterocycles and tropylium cations. This work was a continuation of earlier solid-state studies [18] of tetraphenylborate and its complexation with planar *N*-heteroaromatic cations and tropylium. Investigation was made of tetrakis(4-phenoxyphenyl)-borate (**1**) and tetrakis(biphenyl)borate (**3**) as complexing agents. The complexes were structurally characterized by NMR, and the structures were confirmed by single crystal X-ray diffractometry. In addition to the complexation itself, the further objective was to use these synthesized borates as ionophores in chemical sensors and to evaluate the feasibility of the sensors for the determination of aromatic compounds. Finally, structurally different thiophene monomers with covalently bound molecular recognition sites were synthesized for use in electrochemical sensors.

3.1 Borates

The synthetic protocols for the borates **1**, **3**, and **5** employ three basic steps: 1. formation of aryl magnesium bromide intermediate in the presence of magnesium turnings, 2. quenching of the aryl Grignard reagent with KBF_4 or $\text{BF}_3 \cdot \text{OEt}_2$ to form borate, and 3. aqueous cation exchange. The formation of tetracoordinated sodium tetrakis(4-phenylphenoxy)borate (**2**) and sodium tetrakis(4-phenoxy)borate (**4**) involved reaction of the boron species (sodium tetrahydroborate as boron source) with nucleophilic phenoxy systems in THF. The significant features of the synthesized borate anions in comparison with previously studied TPB^- are the nature of the aromatic units (**1**, **3**, **5**) and the oxygen bridge between boron and the aromatic part (**2**, **4**). In borates (**1**, **2**, and **4**) the oxygen bridges give flexibility to the structure, which could have an effect on the complex formation.

The ^1H , ^{13}C - $\{^1\text{H}\}$, and ^{11}B NMR spectra and the mass spectra verified the borate structures. Details of the characterization of borates are presented in papers I–III.

3.2 Complexes

The complexation of organic molecules via weak, noncovalent interactions such as hydrogen bonding and various π interactions ($\text{CH}\cdots\pi$, $\pi\cdots\pi$ interactions) has received increasing attention during the past decade owing to the significant role of such interactions in recognition processes in biological systems [63]. *N*-Heterocyclic bases, such as imidazole and pyridine, are of great biological importance, and ring systems occur in many natural products. Their complex formation, in both neutral and cationic form, with receptors like crown ethers and ethyl resorcinarene has been studied previously [64,65]. Complexation of the synthesized borates with aromatic nitrogen heterocycles and tropylium was studied as a continuation of our solid-state studies of tetraphenylborate complexes of *N*-heteroaromatic cations [18].

Complexation of borates **1** and **3** with selected aromatic cations was studied to obtain further information about borate complexes. Five cations with delocalized π -systems were chosen on the basis of our previous studies, where they formed complexes with tetraphenylborate. The reaction of tetraphenylborate anion with heterocyclic *N*-acids is also known [18]; it leads to the formation of stable isolable coordination compounds of the type $\text{HetN}^+\text{-B}^-\text{Ph}_3$ and benzene. The reaction evidently proceeds through a metastable Wheland-type intermediate [66].

The precipitation of the complexes usually occurred immediately after mixing of the warmed solutions. X-ray quality single crystals were grown by slow evaporation of the solvent.

3.2.1 Characterization of complexes

Mass and ^1H NMR spectroscopies were used to verify the prepared complex structures. Successfully crystallized complexes were further characterized by X-ray crystallography. Details of the characterization of these complexes are presented in the original papers II and III.

Mass and ^1H NMR spectroscopy

The molecular masses of the borate complexes were determined with measurements of accurate mass peaks. Complexation was observed, and complexes were analyzed by NMR spectroscopy. ^1H spectra gave sufficient data

to identify the products. Characteristic changes in chemical shifts usually occur upon complex formation, providing information on the structure of the complex in solution [4,67,68]. When the standard solution was added to the solutions of tetrakis(4-phenoxyphenyl)borate anion, an upfield shift was observed for all the proton resonances in the aromatic heterocycles except those of the methoxy group of 1-ethyl-4-(methoxycarbonyl)pyridinium cation, where no significant change was observed. The shifts moved gradually with increase in the concentration of the borate. The ^1H NMR spectra of the studied cations thus also provide several signals for independent evaluation of the stability constants.

Crystal structures

Crystallization experiments with selected aromatic nitrogen heterocycles and tropylium were performed with a 1:1 host–guest molar ratio in a suitable solution. Crystal structures were determined for *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**7·1**), 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (**8·1**), tropylium tetrakis(4-phenoxyphenyl)borate (**9·1**), and imidazolium tetrakis(biphenyl)borate (**10·3**). Structures of potassium tetrakis(4-phenoxyphenyl)borate ($\text{K}^+\cdot\mathbf{1}$) and potassium tris[3-(2-pyridyl)pyrazolyl]-hydroborate ($\text{K}^+\cdot\mathbf{6}$) could also be characterized by X-ray crystallography. Hydrogen bonding and $\pi\cdots\pi$ and cation $\cdots\pi$ interactions are the principal attractive forces in the complexes of borates.

Potassium tetrakis(4-phenoxyphenyl)borate ($\text{K}^+\cdot\mathbf{1}$) was crystallized from a mixture of benzene and ethanol. The potassium cations and borate anions form a complex in which each potassium cation is packed between two hosts via strong cation $\cdots\pi$ interactions forming continuous chains of potassium tetrakis(4-phenoxyphenyl)borate (Fig. 8). An interesting feature is that the potassium is located between the inner aromatic rings, i.e. the rings closer to boron, while the outer phenyl rings have no interactions with the cation. The reason for this is the more negative nature of the closer rings and the efficiency of the packing: potassium fits perfectly into the cavity formed by the inner aromatic rings.

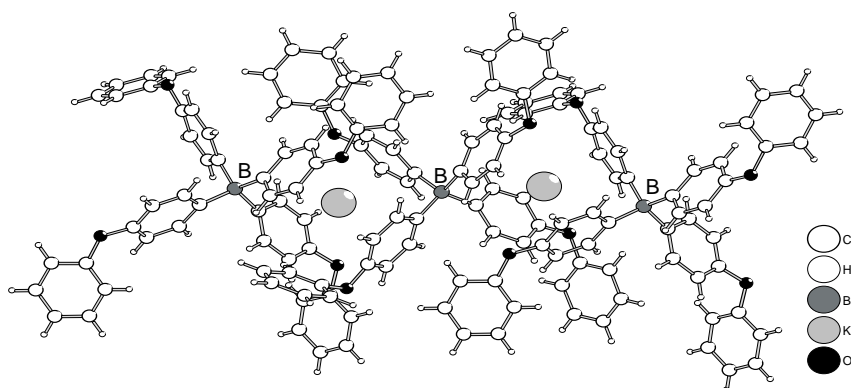


Fig. 8. Crystal structure of potassium tetrakis(4-phenoxyphenyl)borate.

The crystal structures of the planar, aromatic cations with tetrakis(4-phenoxyphenyl)borate (**1**) and tetrakis(biphenyl)borate (**3**) show the importance of π interactions for the complex formation. All structures show relatively short face-to-face $\pi \cdots \pi$ contacts and also edge-to-face C-H $\cdots\pi$ interactions (Fig. 9). In all complexes, most of the interactions of the cation with the anion are with the inner, more negative aromatic rings.

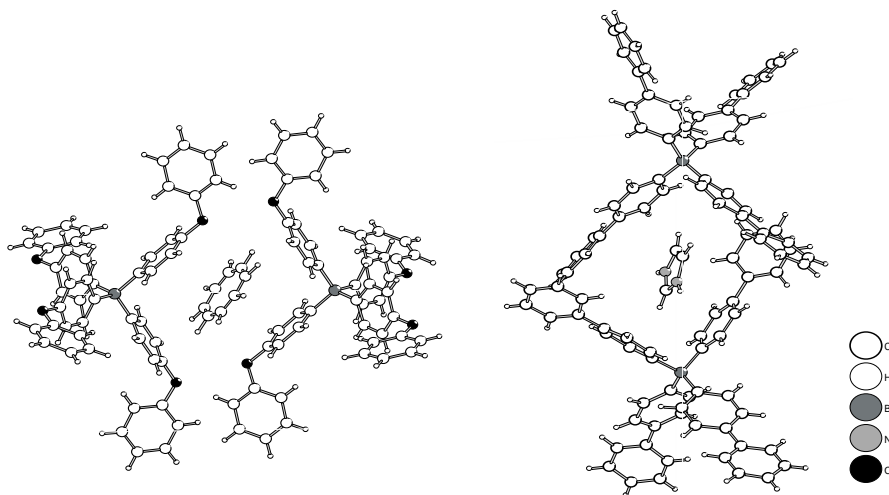


Fig. 9. Crystal structures of tropylium tetrakis(4-phenoxyphenyl)borate (9-1) (left) and imidazolium tetrakis(biphenyl)borate (10-3) (right).

The crystal data for tropylium tetrakis(4-phenoxyphenyl)borate (**9·1**) was obtained from a weakly diffracting crystal crystallized from acetonitrile (Fig. 9). Tropylium is disordered so that it can only be described as an eight-membered ring. Even though the formation of continuous chains of anions mediated by the cations is observed in this case too, here the anions interact with each other. The complex is described by sandwich-type face-to-face packing of the cation and the aromatic rings of the adjacent anions and by edge-to-face interactions between the cation and other aromatic rings of the anion.

N-Methylpyridinium tetrakis(4-phenoxyphenyl)borate (**7·1**) likewise forms continuous chains in which each cation is located between two hosts [II]. The cation–anion interactions are closely similar to ones observed for tropylium tetrakis(4-phenoxyphenyl)borate; i.e. *N*-methylpyridinium is “sandwiched” between two aromatic rings of the adjacent hosts. In addition, there are edge-to-face $\pi\cdots\pi$ interactions with two other rings. As in the potassium structure, the cation is located in the cavity formed by the inner rings, and the outer rings do not interact with the cation. Instead, the outer aromatics are edge-to-face connected to nearby anions, joining the adjacent chains together.

1-Ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate complex (**8·1**) deviates most from the other complexes. Here the cation interacts with more than two anions and even slightly with the outer aromatics of the anion owing to the extended side chains and therefore larger size of the cation [II]. However, the primary and strongest intermolecular interactions, as before, are the slightly offset face-to-face type of $\pi\cdots\pi$ interactions between the cation and two adjacent anions and the edge-to-face interactions. No clear chain- or column-type of packing is observed in this case.

The only tetrakis(biphenyl)borate (**3**) structure that was successfully crystallized was imidazolium tetrakis(biphenyl)borate (**10·3**), which was obtained from ethanol solution (Fig. 9). Imidazolium is somewhat smaller than the other cations used in the study, and tetrakis(biphenyl)borate (**3**) a more rigid anion than tetrakis(4-phenoxyphenyl)borate (**1**); hence the properties and interactions of this structure are slightly different. Imidazolium is also complexed by π interactions, but instead of sandwich-type face-to-face $\pi\cdots\pi$ interactions, imidazolium is offset face-to-face stacked with one of the inner phenyl rings. There are also some π interactions to the outer aromatic rings of the anion. Owing to the rigid nature of the anion and small size of the cation, the packing of the anion–cation adducts is not as efficient as with tetrakis(4-phenoxyphenyl)borate. The packing is still similar to that of other complexes, however, being also a chain-like assembly of

anions and cations. The preferred mode of interaction between the aromatic rings is offset stacked or T-shaped, edge-to-face orientation (Fig. 10). The preferred geometries for interactions between the aromatic rings have been explained with use of a model for the charge distribution in an aromatic π system [69]. Both edge-to-face and offset stacked geometry were observed in complexes of borate anions in this study.

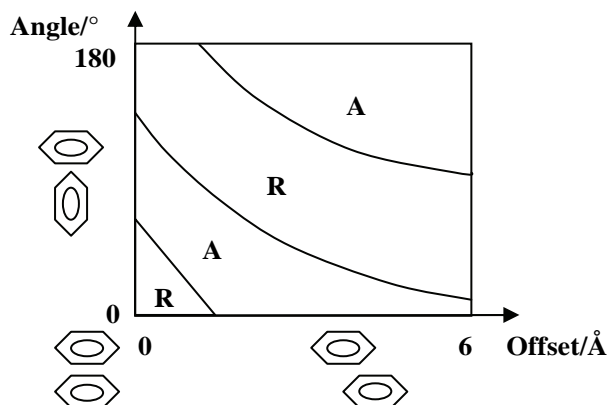


Fig. 10. Interaction between idealized π -atoms as a function of orientation: two attractive (A) geometries and the repulsive (R) face-to-face geometry are illustrated [69,70].

Crystals of potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate ($K^+\cdot\mathbf{6}$) were obtained from methanol–acetonitrile solution containing potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate and *N*-methylpyridinium iodide. Tris[3-(2-pyridyl)pyrazolyl]hydroborate (**6**) is a tris-chelating hexadentate podand ligand with two of the bidentate arms two-coordinated to a potassium cation and the third arm to the adjacent potassium. In other words, each potassium cation is hexacoordinated to six nitrogens of two different hosts, and one-dimensional continuous chains of complexes are thereby formed [III]. The polymeric chains are connected via edge-to-face and face-to-face $\pi\cdots\pi$ interactions.

3.2.2 Stability of complexes

The stability constants of *N*-methylpyridinium (**7**) and 1-ethyl-4-(methoxycarbonyl)pyridinium (**8**) with borate **1** were measured by ^1H NMR titration in acetonitrile–methanol solution [II]. The mixture of solvents was chosen because

methanol increases the solubility of tetrakis(4-phenoxyphenyl)borate (**1**), and comparison with the previously studied tetraphenylborate systems is then possible. Since tropylium decomposes in the presence of alcohol, the stability constant of the tropylium complex could not be measured in CD₃CN/CD₃OD solution [71].

A standard solution of guest in deuterated acetonitrile and deuterated methanol (1:1 by volume) was prepared with a concentration of 2×10^{-3} M, just sufficient to give an observable NMR signal. A series of donor solutions (0.01–1.0 M) were made by weighing out an appropriate amount of donor. A 2-ml portion of the standard solution was then added and the flask was re-weighed. The solutions were mixed thoroughly and the spectrum was measured immediately. Five-millimeter NMR tubes sealed with parafilm to avoid evaporation were used. The temperature (303 K) was held constant during the measurements. The stability constant *K* for the complexation was calculated from NMR chemical shifts using the Benesi-Hildebrand least-squares line-fitting procedure (Fig. 11).

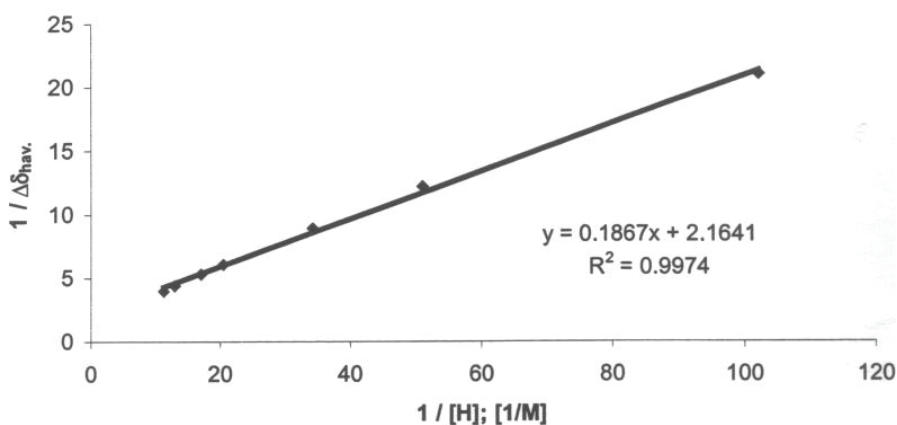


Fig. 11. Benesi-Hildebrand plot according to equation 4 for a system undergoing fast equilibration.

In each case the differences in chemical shifts of the free and complexed cations are a linear function of the inverse borate concentration ($1/[\text{borate}]$) indicating 1:1 stoichiometry. The stability constant for *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate (**7·1**) is $12 \pm 2 \text{ dm}^3\text{mol}^{-1}$, and that for 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate (**8·1**) is $13 \pm 1 \text{ dm}^3\text{mol}^{-1}$. There are no significant differences between these and the stability

constants for complexes of tetraphenylborate (with these cations 17 ± 2 and $10 \pm 1 \text{ dm}^3\text{mol}^{-1}$, respectively) measured in our previous studies [18]. Measurements were also done earlier for imidazolium and 1-methylimidazolium tetraphenylborates (19 ± 4 and $46 \pm 2 \text{ dm}^3\text{mol}^{-1}$, respectively), and the stability constants of these complexes are likewise about the same as those measured here. Also in the present study, polar solvent (methanol) has its own impact on the complexation environment. It increases the solubility of the charged species, while decreasing the degree of association of the complexes, which together lead to lower stability constants.

As a complexing agent, tetrakis(4-phenoxyphenyl)borate (**1**) differs from tetraphenylborate in that the additional phenyl rings could potentially take part in the binding and even encapsulate the cation. Borate **1** also contains electronegative oxygens, which make the structure flexible and provide a hydrogen bonding site for hydrogen-bonding guests. However, the similarity of the stability constants suggests that these two structural features do not have a significant positive impact on the complexation. In addition, the crystal structures show that the cations are situated in the cavity formed by the inner aromatic rings, closer to boron, and have no interactions with the outer rings. These findings are in agreement with the similarity of the stability constants to those of the tetraphenylborate complexes.

3.3 Thiophene derivatives

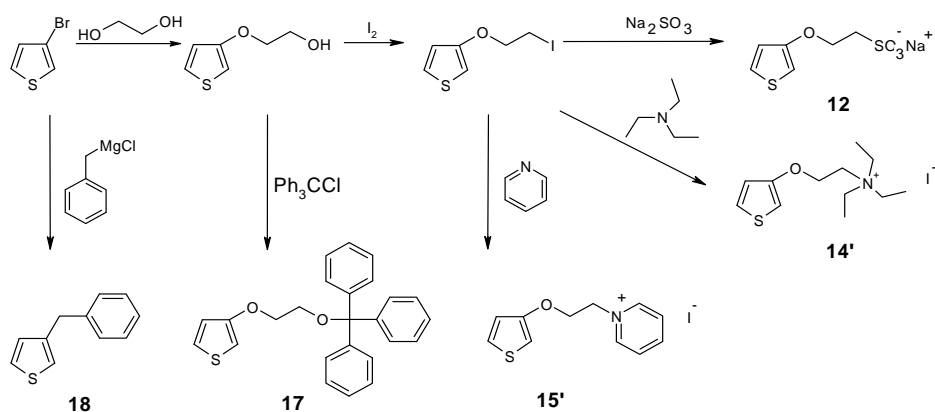
Heteroaromatic polythiophene has the disadvantage of being insoluble, which limits the development of applications. As a means of overcoming this problem, numerous substituted derivatives of this polymer have been developed, carrying alkyl, alkoxy, aryl, or other substituents along the backbone [72,73,74,75]. Substitution, for instance at the 3 position, with various substituents has led to materials that are soluble in common organic solvents and even water. Through control of the main-chain architecture and pendant group chemistry, a broad variety of properties have been made available from the parent system.

Modification of the receptor part in the monomeric structure through immobilizing units selective to a particular analyte involves supramolecular chemistry. A number of structural features can be used in the design of ionophores for ion-selective electrodes [76].

3.3.1 3-Substituted thiophenes

The synthesis of 3-substituted thiophenes is of special interest in view of the demonstrated potential of polythiophenes as organic conductors. In particular, the importance of alkoxy substituents has been pointed out [77]. Aromatic nucleophilic substitution is one of the most straightforward methods employed to functionalize aromatic rings and obtain aryl ethers. [78]

An alkoxy thiophene, 2-(3-thienyloxy)ethanol, was prepared from 3-bromothiophene and the appropriate sodium alkoxide in the presence of copper oxide and potassium iodide using conditions developed by Gronowitch [79] (Scheme 1). Through conversion of alcohol into alkyl halide with triphenylphosphine, iodine, and imidazole, compounds sodium 2-(3-thienyloxy)ethanesulfonate (**12**) [IV], 2-(3-thienyloxy)ethyltriethylammonium iodide (**14'**), and 2-(3-thienyloxy)ethylpyridinium iodide (**15'**) were prepared.

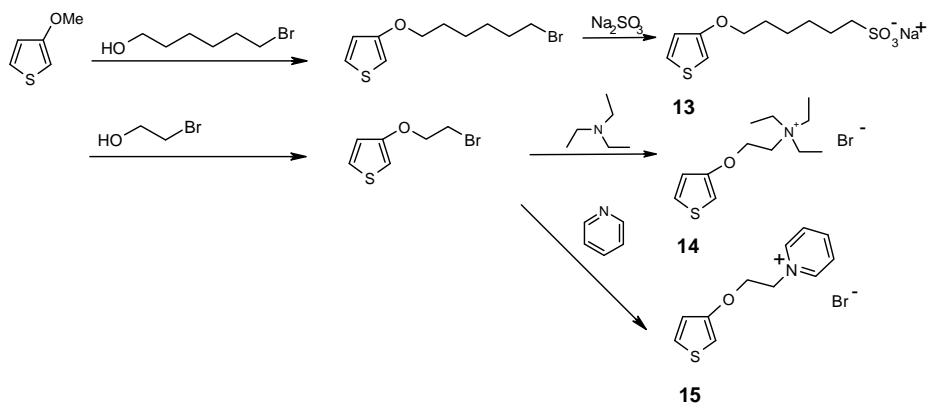


Scheme 1. Synthetic routes for sodium 2-(3-thienyloxy)ethanesulfonate (**12**), 2-(3-thienyloxy)ethyltriethylammonium iodide (**14'**), 2-(3-thienyloxy)ethylpyridinium iodide (**15'**), 3[2-((triphenylmethyl)oxy)ethoxy]thiophene (**17**), and 3-benzylthiophene (**18**).

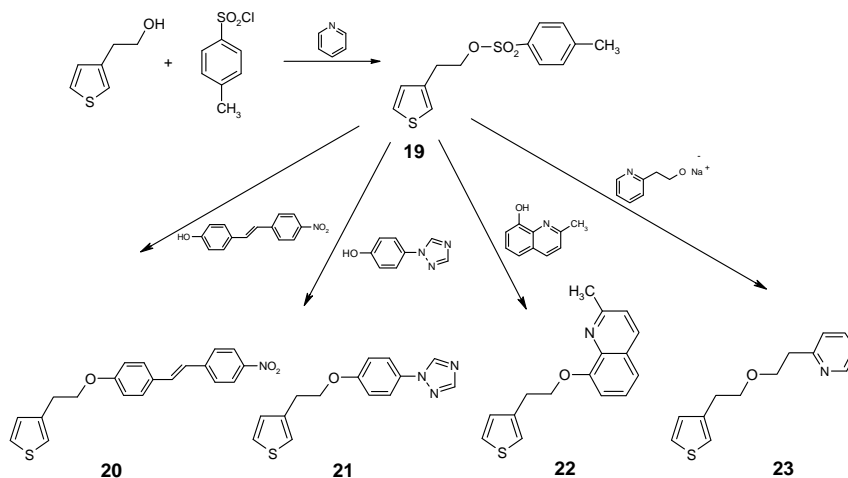
Monomer (**18**), 3-benzylthiophene, having a phenyl alkyl substituent, was synthesized using a Grignard reaction (Scheme 1). The trityl ether derivative (**17**) was synthesized by reaction of 2-(3-thienyloxy)ethanol with trityl chloride in pyridine solution.

2-(3-Thienyloxy)ethyltriethylammonium bromide (**14**), 2-(3-thienyloxy)ethylpyridinium bromide (**15**), and sodium 6-(3-thienyloxy)hexanesulfonate (**13**) [IV] were prepared by a modification of procedures described in the literature [46,47].

The monomers were obtained in two steps from 3-methoxythiophene (Scheme 2). In addition, 2-(3-thienyloxy)ethanesulfonate was synthesized by the same method.



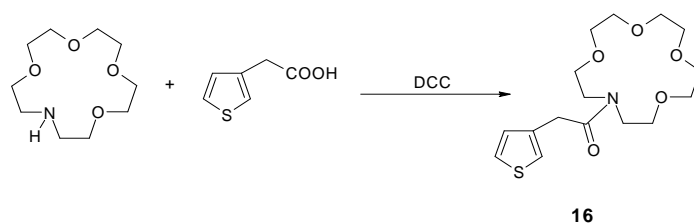
Scheme 2. Synthetic routes for sodium 6-(3-thienyloxy)hexanesulfonate (13), 2-(3-thienyloxy)ethyltriethylammonium bromide (14), and 2-(3-thienyloxy)ethylpyridinium bromide (15).



Scheme 3. Synthetic routes for 3-[2-(toluenesulfonyl)ethyl]thiophene (19), 3-[2-(4-oxy-4'-nitrostilbene)ethyl]thiophene (20), 3-[2-(4-oxy-1,2,4-triazol-1-yl)ethyl]thiophene (21), 3-[2-(8-oxy-2-methylquinoline)ethyl]thiophene (22), and 3-[2-(2-pyridine-ethoxy)ethyl]thiophene (23).

The preparation of 3-[2-(toluenesulfonyl)ethyl]thiophene (**19**), 3-[2-(4-oxy-4'-nitrostilbene)ethyl]thiophene (**20**) [53], 3-[2-(4-oxy-1,2,4-triazol-1-yl)ethyl]thiophene (**21**), 3-[2-(8-oxy-2-methylquinoline)ethyl]thiophene (**22**), and 3-[2-(2-pyridine-ethoxy)ethyl]thiophene (**23**) is shown in Scheme 3. The alcohol was converted to a tosylate, which served as precursor for the products. The intermediate tosylate was obtained by the reaction of 2-(3-thienyl)ethanol with tosyl chloride in pyridine solution and was pure enough to be used as obtained.

The synthesis of monomer (**16**), having a cyclic substituent, proceeded by the reaction of dicyclohexylcarbodiimide, DCC, with carboxylic acid to form an ester. 1-Aza-15-crown-5 nucleophile reacts with this ester, expelling urea as a leaving group (Scheme 4).



Scheme 4. Synthetic route for thiophene 3-substituted by azacrown ether (16**).**

Cyclic and open-chain structures have different properties as complexing agents. The electrochemical recognition of ions by macrocyclic receptors that contain an electrochemically responsive signalling function is an active field of research. The size of the cyclic receptor is important for selectivity. A common group of cyclic complexing agents is the crown ethers. Crown ethers are well known for their ability to make complexes with alkali metal cations. The stability of the crown ether – metal complex is dependent on the number of ether donor atoms in addition to the cavity size and shape relative to the cation to be recognized [80]. [18]Crown-6 ether is a good receptor for the protonated *N*-terminus of an amino acid and for potassium cation. Inserting atoms (other than oxygen) or functionality may improve the affinity of these compounds toward target molecules or ions [81]. Taking advantage of the properties of crown ethers and the conductive features of thiophenes should allow the construction of selective and reversible ion sensors. Similarly, azacrown ethers, which are known for their selective complexing properties toward alkaline cations, can be grafted onto the polypyrrole [49] or polythiophene backbone. Arms, added to either the carbon or the nitrogen atoms of azacrowns, will strengthen the binding ability to

cations. The monomer synthesis in this work involved the condensation of 3-thiopheneacetic acid and azacrown ether following a known procedure [48]. Catenanes and rotaxanes are other representative cyclic compounds in supramolecular chemistry. Typical linear components encountered in supramolecular chemistry include podands, which are known for their ability to wrap around metal and lanthanide ions [82,83], and different tripod molecules, which are compounds where three arms containing the donor atoms are connected to a nitrogen atom [84,85].

Molecular basket- or cage-like structures, such as calixarenes, can interact with cations, anions, and neutral structures. Interaction is determined by the functional groups bonded to the basic skeleton. Calixarene-based potentiometric ion sensors can be divided into main group, transition metal, and lanthanide selective ion sensors [86].

Of the compounds mentioned above, which are commonly encountered in supramolecular chemistry, only some (Fig. 12) were used here in the construction of potentiometric ion-selective electrodes. With the focus of the present work on specific applications of supramolecular chemistry, host-guest and weak interactions were of special interest. Many heterocyclic compounds derived from imidazole, pyrazole, or pyridine possess versatile coordination properties [87]. Pyridine-based ligands are common in the transition metal complexes used in molecular recognition and host-guest chemistry. Pyridine groups enhance the capability of ligands for attractive π -stacking. Heterocyclics can act as monodentate or bidentate ligands. Phenols in structures like 3[2-((triphenylmethyl)oxy)ethoxy]thiophene (**17**) and 3-benzylthiophene (**18**) readily engage in $\pi\cdots\pi$ interactions and provide greater specificity for molecules containing aromatic groups. The quinoline group can bind metal through both nitrogen and oxygen donor atoms [88,89].

Another important parameter is the charge of the receptor unit. Negative charge in the receptor unit should increase stability in the complexation of metal cations. In addition, a covalently bound, charged ion-recognition site also functions as a counteranion to the positively charged conjugated backbone after electropolymerization. Positive charge can be used to increase the affinity for anions. Neutral structures were prepared to obtain information about complexation in the absence of ion-pair formation or electrostatic interactions.

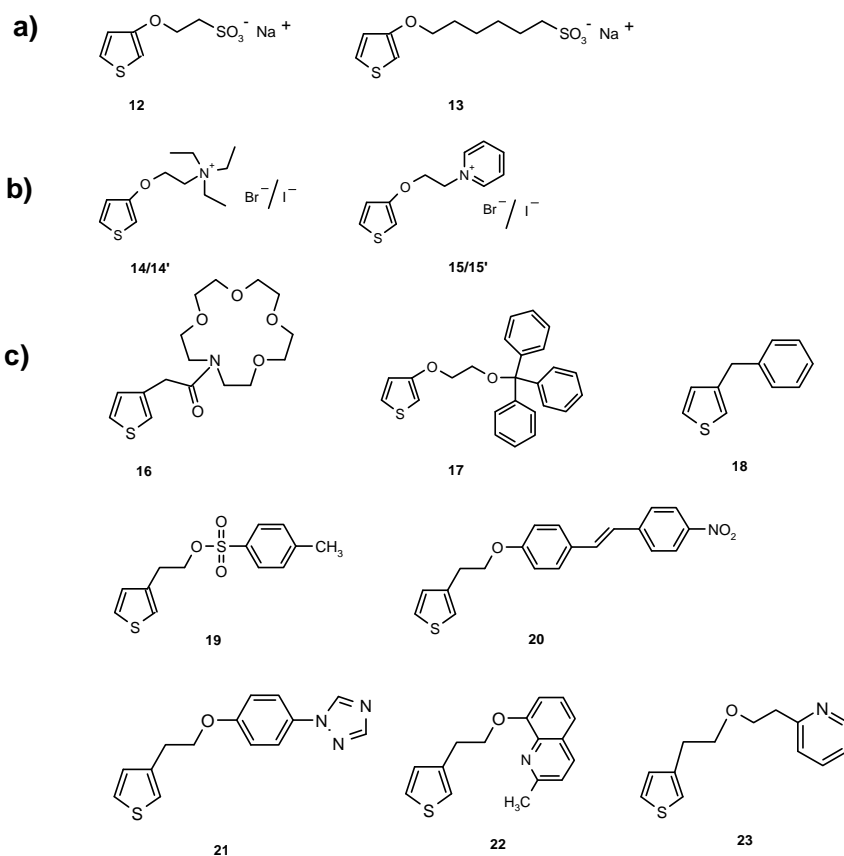


Fig. 12. 3-Substituted thiophenes synthesized in this work, with a) anionic ion-recognition sites b) cationic ion-recognition sites, and c) neutral ion-recognition sites.

In complexation with organic molecules, typical forces that determine the strength and selectivity of the complexes are, among others, hydrogen bonding and $\pi \cdots \pi$ or cation $\cdots\pi$ interactions. The growing number of reports on the design of ion-selective devices is practical proof of the interest in this field. 3-Substituted thiophene monomers synthesized during this work for study of the electrochemical properties, selectivity, and sensitivity they produce in ion-selective electrodes are presented in Fig. 12.

Traditional one-dimensional ^1H NMR spectroscopy was sufficient to provide information on the structure and chemical shifts of 3-substituted thiophenes. In addition, elemental analysis or exact mass peaks were used for the characterization. $^{13}\text{C}\{-^1\text{H}\}$, DEPT, and HMBC spectra were measured where

needed. Figure 13 presents selected spectra. Protons of the thiophene ring appeared as three separate signals in the range of 7.5–5.8 ppm.

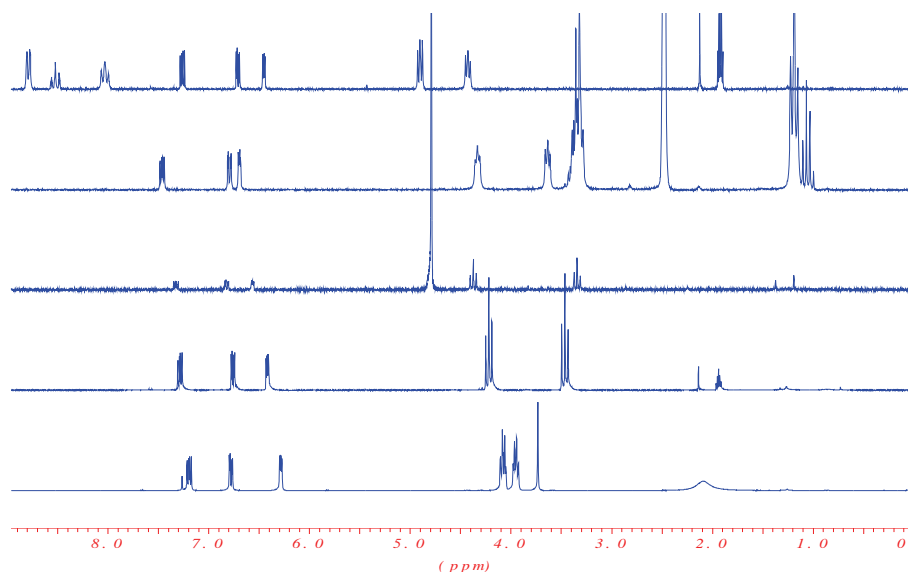
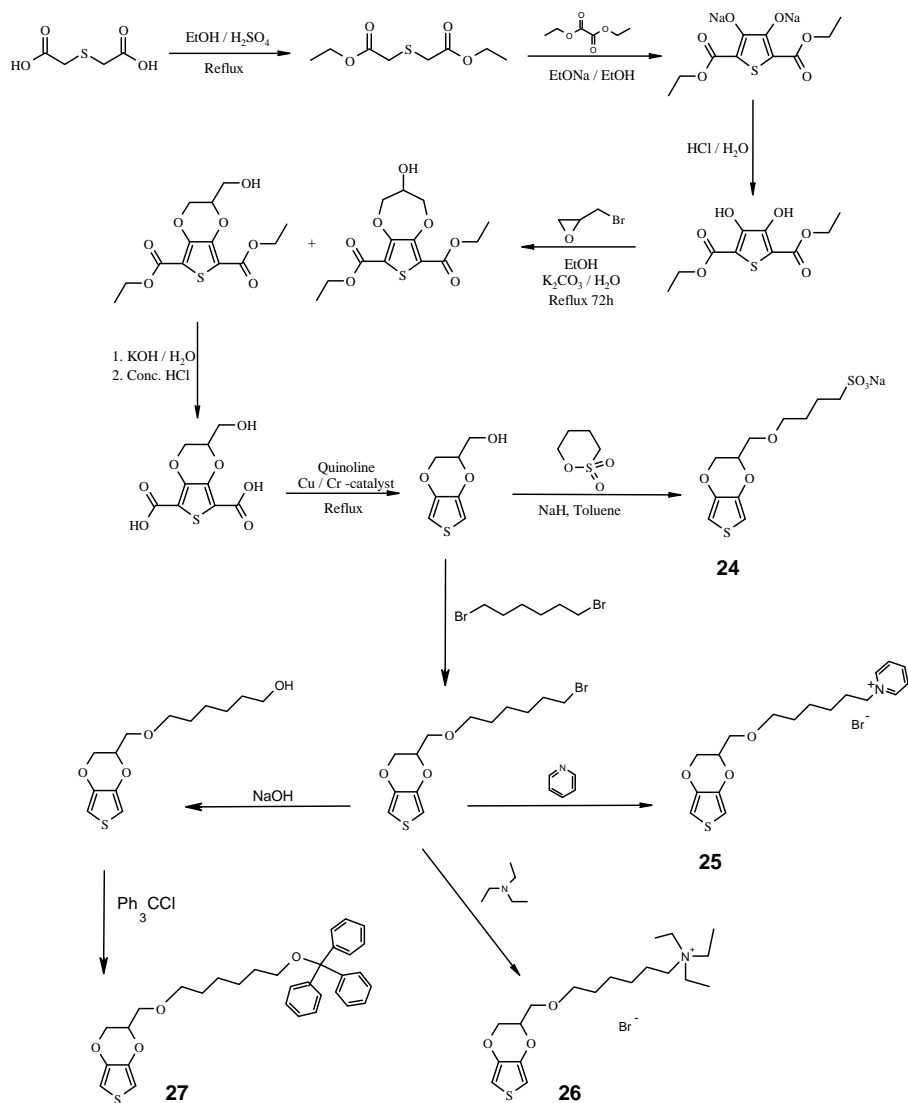


Fig. 13. From bottom to top, spectra of 2-(3-thienyloxy)ethanol, 3-(2-iodo)ethoxythiophene, 2-(3-thienyloxy)ethanesulfonate, 2-(3-thienyloxy)ethyltriethylammonium iodide, and 2-(3-thienyloxy)ethylpyridinium iodide. Protons of the thiophene ring can be seen in the range of 7.5–5.8 ppm.

3.3.2 3,4-Ethylenedioxythiophene derivatives

Hydroxymethyl-EDOT monomer, which was used as the precursor for EDOT derivatives, was synthesized in a six-step synthesis starting from thiodiglycolic acid (Scheme 5) [56]. Acid-catalyzed esterification and condensation with diethyl oxalate gave the disodium salt, which was then acidified with hydrochloric acid. The reaction of epibromohydrin with the dihydroxythiophene derivative in the presence of potassium carbonate as a catalyst yielded a mixture of two isomers: hydroxymethylated 3,4-ethylenedioxythiophene and hydroxylated 3,4-propylenedioxythiophene, ProDOT, 90:10. The desired six-membered ring can be separated from its seven-membered isomer by chromatography. The next steps involved hydrolysis of ester groups and decarboxylation of 2-(hydroxymethyl)-2,3-

dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxylic acid at high temperature in quinoline using copper chromite catalyst.



Scheme 5. Synthetic routes for 3,4-ethylenedioxythiophene (EDOT) derivatives (24-26) synthesized in this work.

Hydroxymethyl-EDOT was subsequently converted to the water-soluble sodium salt of the butanesulfonic acid-functionalized EDOT (**24**) and alkoxy-substituted EDOT derivatives (**25–27**). The synthesis of **24** is based on the reaction between an alcohol group of the thiophene derivative and butanesultone as sulfonated reagent in toluene [57]. The product (**24**) was precipitated in acetone washed with hot acetone to remove any unreacted material, and dried under vacuum with the aid of a water bath. 2-[(6-Bromohexyl)oxymethyl]-2,3-dihydrothieno[3,4-b][1,4]dioxin was obtained by alkylation of hydroxymethyl-EDOT with an excess of 1,6-dibromohexane (NaH, THF, 0 °C). Monomers **25**, **26**, and **27** were prepared from this by procedures similar to those described in section 2.2.3 for 2-(3-thienyloxy)ethyltriethylammonium bromide (**14**), 2-(3-thienyloxy)ethylpyridinium bromide (**15**), and 3[2-((triphenylmethyl)oxy)-ethoxy]thiophene (**17**).

As mentioned above, replacing thiophene by EDOT takes advantage of the lower oxidation potential. While possible for thiophenes, however, direct functionalization of EDOT is not possible and it is necessary to redo the whole multistep procedure of the EDOT system, as described in Scheme 5, to obtain a functionalizable starting material. Long synthetic procedures and poor yields in the preparation of hydroxymethyl-EDOT are major obstacles in using this derivative as the material of choice. Partly because of these problems, functionalization of EDOT based on this approach has been limited to substituents of simple structure such as alkyl, alkylsulfonate, and oligooxyethylene chains [28,90]. Some recent exceptions are cyanobiphenyl- [91], ferrocene- [92] and dendronized-derivatized EDOT [93].

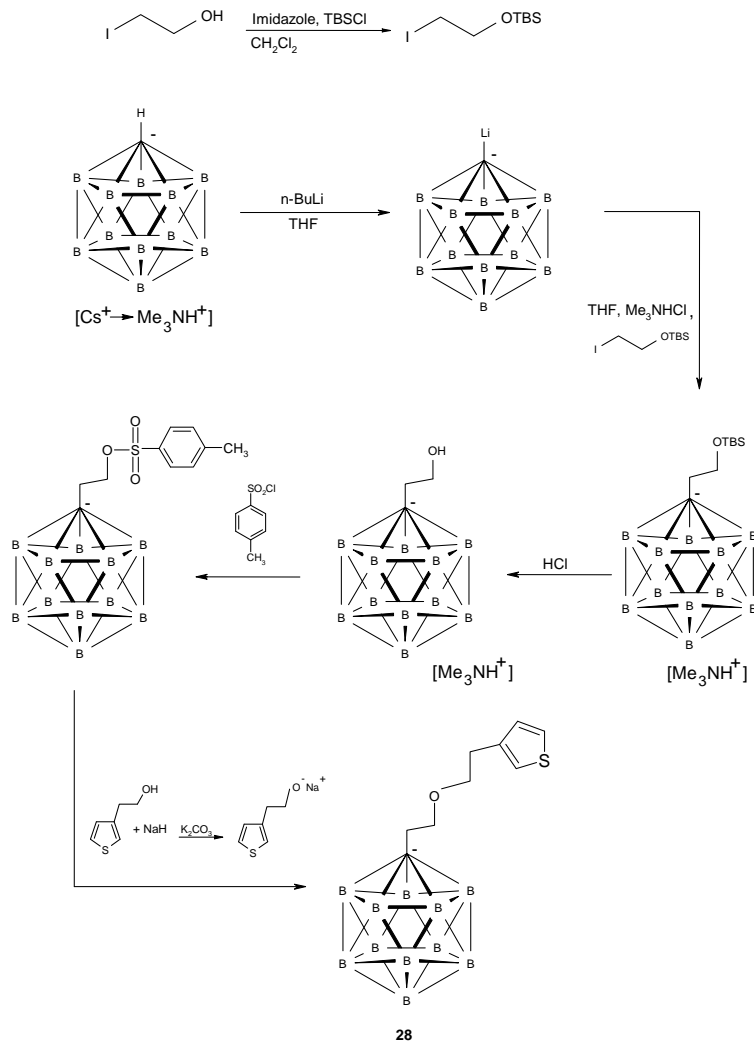
¹H NMR and mass spectroscopy provided sufficient information for characterization of the 3,4-ethylenedioxythiophene (EDOT) derivatives. The molecular masses of the monomers were verified with measurements of accurate mass peaks. The yields of the products (**24–27**) were relatively low (27–77%).

3.3.3 Thiophene 3-substituted by carborane

For several decades now, tetraphenylborates have been the lipophilic anions in ion sensors. There are, however, several inherent disadvantages associated with their use, such as susceptibility toward oxidants, light, and hydrolysis by acids [19,94,95]. Carboranes are a relatively new class of weakly coordinating anions based on a stable boron cluster framework (CB₁₁H₁₂⁻) [96]. The weak coordination and ion-pair formation properties of carboranes, due to the lack of

electron lone pairs and π -electrons, make them attractive for ion-sensing applications [97]. Solid-contact ISEs based on plasticized PVC membranes containing carborane as negatively charged groups have already been studied as potentiometric sensors for organic cations by the group at Åbo Akademi University [20].

The idea behind the present work with carborane-substituted thiophenes was to prevent ionophore loss and to improve the operational time of the ion sensor through covalent attachment of both the ionophore and the anionic site to the thiophene monomer. After conversion of cesium carborane into a trimethylammonium salt, butyllithium was added to produce a soluble form of the C-lithio derivative (Scheme 6). Butane and trimethylamine were removed by evaporation. Treatment of the lithiated compound with *tert*-butyldimethylsilyl chloride, TBSCl, protected with 2-iodoethanol [98] led to the C-alkyl derivative, which was precipitated by the addition of trimethylammonium chloride. After removal of the protecting group by acid hydrolysis, compound $[\text{Me}_3\text{NH}][\text{HO}(\text{CH}_2)_2\text{-CB}_{11}\text{H}_{11}]$ was converted to a tosylate in pyridine solution. The tosylate derivative was reacted with sodium alkoxide of 2-(3-thienyl)ethanol to obtain the polymerizable carborane anion. The final product contained minor amounts of impurities, as observed in the NMR spectra. The quantity of sample available was not sufficient for further purification.



Scheme 6. Synthetic route for carborane derivative (**28**) synthesized in this work.

Covalent attachment of active sensing components to thiophene polymers represents a promising route for the improvement of ion sensors. Leaching of lipophilic anionic additives from sensor membranes into aqueous solution should thereby be reduced.

3.4 Applications in ion-selective electrodes

The most important process of an ion-selective electrode is molecular recognition, i.e., the detection of a certain species in the presence of other species, realized through a specific ionophore immobilized in the ion-selective membrane [30]. If the ionophore reacts specifically with the analyte, it gives the sensor qualitative information about the sample being analyzed. Our study concentrated on the synthesis of ion-recognition molecules to be incorporated in the membrane or directly covalently attached to the polymer chain. The research work was divided in such a way that the synthesis of borates as ion-recognition sites and of monomers with sensing groups for electropolymerization into conductive polymers were carried out in Oulu, while the electropolymerization and sensor characterization were done by Prof. Ivaska's group at Åbo Akademi University.

Sensors can be based either on the solid-contact principle as with plasticized PVC-based ion-selective membranes (Fig. 4) or on the concept of conductive polymer where both the ion-recognition site and the charge-compensating ion are covalently bound to the conductive polymer structure forming the sensing membrane (Fig. 14). The latter is of great potential for the future development of durable and miniaturized ion sensors [31] and the ultimate goal of this whole project. It is also possible to bind ion-recognition sites electrostatically to the sensing membrane.

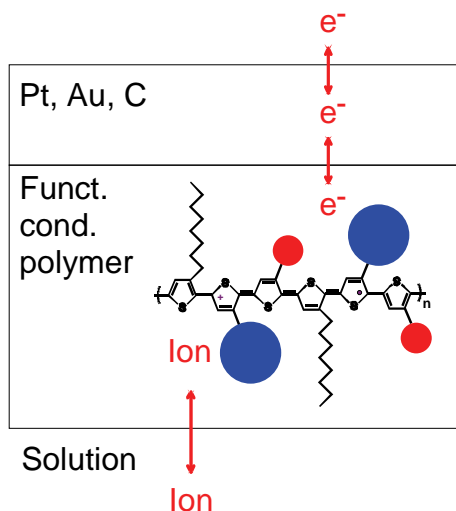


Fig. 14. Ion-selective electrode based on conductive polymer (CPSE) [38,99].

3.4.1 Borate derivatives in ISEs

At the start of this work, aromatic cations like *N*-methylpyridinium, tropylium, and imidazolium had been demonstrated to form complexes with borates [18]. Crystal structure analyses had given evidence of cation $\cdots\pi$ interactions and $\pi\cdots\pi$ and hydrogen bond interactions. With these results in hand, the research was focused on the synthesis of new ionophores based on borate derivatives and their application in chemical sensors for aromatic cations and metal ions. The responses of the chemical sensors to heterocyclic cations were studied at Åbo Akademi University. The results indicated the importance of π interactions, for instance in the structure of tetraphenylborate-based ionophores, between aromatic cations and the membrane components (phenyl groups). Noncovalent interactions can be exploited in the design of ISEs that are selective to aromatic cations.

It was of particular interest to vary the aryl substituents in borate anions to determine their influence on the sensitivity and selectivity of ion-selective electrodes (ISEs) toward aromatic cations and metal ions. Anionic borate derivatives synthesized within this project together with some commercially available derivatives were studied as charged ion-recognition sites, included as ion receptors (charged carriers) in plasticized PVC membranes where 2-nitrophenyl octyl ether (*o*-NPOE) or bis(2-ethylhexyl)sebacate (DOS) was used as plasticizer. Tetrakis(4-phenoxy)borate anion could not be evaluated due to its limited solubility in THF, which was used to dissolve the membrane components. It was also of interest to evaluate the above charged and some neutral carriers containing aromatic anthryl groups as ionophores in ISEs for aromatic cations.

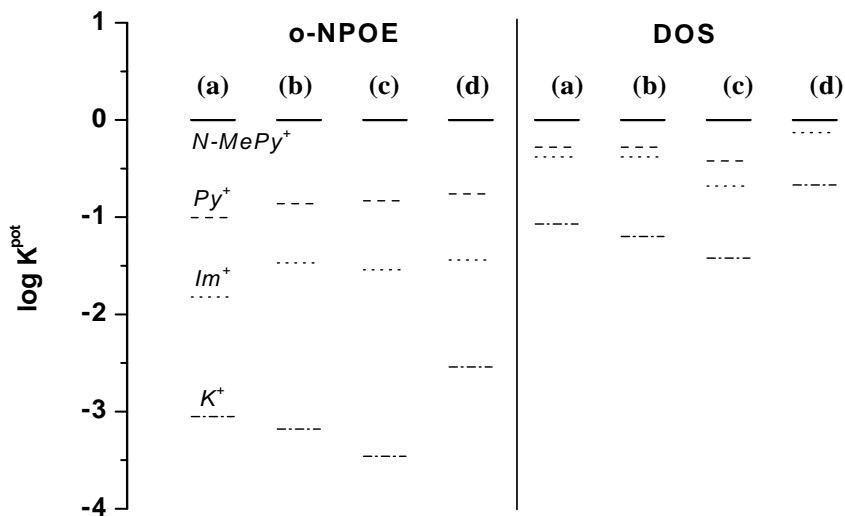


Fig. 15. Selectivity of solid-contact ISEs based on charged carriers: (a) tetraphenylborate, (b) tetrakis(4-fluorophenyl)borate, (c) tetrakis(4-chlorophenyl)borate, (d) tetrakis(4-phenoxyphenyl)borate, with *o*-NPOE or DOS as plasticizer. Ions were *N*-methylpyridinium, pyridinium, imidazolium, and potassium [1].

The potentiometric responses were compared for solid-contact ISEs based on different charged carriers, with *o*-NPOE or DOS as plasticizer and poly(3,4-ethylenedioxythiophene) PEDOT(PSS) as solid contact material. The potentiometric selectivity coefficients ($\log K^{pot}$) are summarized in Fig. 15. Electrodes were calibrated in solutions of *N*-methylpyridinium, which was used as model aromatic cation in studying the mechanism of molecular recognition. As can be seen, all ISEs were more selective to *N*-methylpyridinium (*N*-MePy⁺) than to the other cations tested. Good selectivity was observed for the ISE based on tetrakis(4-chlorophenyl)borate anion (c in Fig. 15) with *o*-NPOE as plasticizer (more polar than DOS). Also the other borate derivatives exhibited selectivity to the aromatic heterocyclic cations distinguishing between the studied alkali and alkaline earth metals. As can be seen in Table 1, selectivity was best toward *N*-methylpyridinium cation, followed by pyridinium, imidazolium, lithium (Li⁺), sodium (Na⁺), potassium (K⁺), ammonium (NH₄⁺), calcium (Ca²⁺), and magnesium (Mg²⁺). The selectivity of ISEs is influenced by both the charge carrier (ionophore) and the plasticizer.

Table 1. Potentiometric selectivity coefficients ($\log K^{pot}$) for ISEs [I,II].

<i>j</i>	$\log K_{N-MePy, j}^{pot}$						
	(1)	(2)	(3)	(5)	TPB ⁻	TpFPB ⁻	TpCIPB ⁻
Li ⁺	-3.0	-0.7	-3.4	-3.1	-2.8	-3.2	-3.4
Na ⁺	-3.1	-0.7	-3.3	-3.1	-2.7	-3.1	-3.3
K ⁺	-2.6	-0.7	-2.4	-2.7	-2.9	-3.1	-3.6
NH ₄ ⁺	-2.6	-0.5	-3.0	-3.0	-2.9	-3.0	-3.3
Ca ²⁺	-4.2	-1.7	-4.9	-4.5	-4.0	-3.0	-3.5
Mg ²⁺	-4.1	-1.6	-4.7	-4.6	-4.0	-4.2	-5.2
Py ⁺	-0.6	0.8	-1.1	-0.6	-1.5	-4.2	-5.1
TMA ⁺ [a]	-0.4	-0.4	-0.7	-0.1	-0.4	-1.0	-0.9

[a] TMA⁺ tetramethylammonium. TpFPB⁻ tetrakis(4-fluorophenyl)borate (sodium) and TpCIPB⁻ tetrakis(4-chlorophenyl)borate (potassium) were commercial reagents.

In compounds **1**, **3**, and **5**, boron is bound to four aryl groups, while in compound **2** it is bound to four oxygens. The species bound has a marked effect on the ion sensitivity. When oxygen is located further away from boron, it has only a minor effect on the ion-recognition process. The results indicate that the substituents closest to boron play a determining role in the ion-recognition of *N*-methylpyridinium by aromatic borate anions. Detailed comparison further shows that the nature of the aromatic unit bound to boron has some effect on the selectivity. It is noteworthy that the ISE based on borate **2** shows significantly higher selectivity to pyridinium than to *N*-methylpyridinium cation, despite the greater lipophilicity of the latter. This indicates some specific interactions between **2** and pyridinium cations. Since the selectivity of the various ion exchangers differs by about one order of magnitude, the results show that the structure of the ion exchanger may play a significant role in the ion-recognition process if no other ionophore is present in the membrane.

The influence of the plasticizer was investigated with tetrakis(4-phenoxyphenyl)borate. In a study of the response of potentiometric sensors (ISEs) to local anesthetics (aromatic cations bupivacaine, lidocaine, and procaine), the selectivity sequence was found to follow the lipophilicity of the cation. These arylalkylamines were in the form of their hydrochloride salts. “Dummy” membranes based solely on PVC and plasticizer (DOS or *o*-NPOE) were sensitive to bupivacaine. Addition of the tetraarylborate derivative (ionophore) improved the selectivity for membrane with *o*-NPOE as plasticizer but had a negligible influence on membranes with DOS. These results show that substituted borates offer interesting possibilities for the design of new charged

carriers to be used in cation-selective electrodes. The choice of borate derivative influences the selectivity, but this also depends on the plasticizer.

Tetrabutylammonium tetrabutylborate ($\text{TBA}^+ \text{TBB}^-$) was studied as ionophore in ion sensors for a non-aromatic negatively charged model compound and compared with the performance of borate derivatives studied previously. The sensor based on $\text{TBA}^+ \text{TBB}^-$ gave a cationic response to $\text{TBA}^+ (\text{Cl}^-)$ salt and an anionic response to tetraphenylborate anion (Na^+ -salt) but did not respond to the less lipophilic *N*-methylpyridinium cation or alkali metal ions. From these results it can be concluded that the non-aromatic control anion should preferably be in the form of an alkali metal salt, e.g. sodium tetraoctylborate. The ion in solution that is more lipophilic will determine not only the selectivity but also the anionic/cationic sensitivity.

Attention was also paid to the behavior of some neutral molecules, such as cyclophanes and resorcarenes, as ionophores. Cyclophanes did not improve the selectivity over that of borates. Neutral anthryl-containing structures have only slight influence on the selectivity as compared with the lipophilic tetrakis-(4-chlorophenyl)borate anion alone. The presence of resorcarene in ion sensors made them as selective to pyridinium as to *N*-methylpyridinium, which means that resorcarene interacts specifically with pyridinium. With tetraphenylborate as ionophore, selectivity to *N*-MePy⁺ was about ten times the selectivity to pyridinium cation.

Among the ionophores tested so far, the borate derivatives showed the best selectivity to *N*-methylpyridinium, which was used as a model compound for aromatic cations. These results strongly indicate that sensors for aromatic cations can be based on borate derivatives, but the selectivity also depends on the plasticizer. Possibly the selectivity could be further improved by combining borates and other complexing functional groups in the same molecule. This might allow hydrogen bonding, for example, in addition to electrostatic and π interactions. Borate derivatives open up new avenues for the selective molecular recognition of cations by ion-selective electrodes.

3.4.2 Thiophene derivatives in ISEs

Thiophene and EDOT derivatives were prepared as functionalized monomers for use in sensor studies. There are many ways to modify the monomer and receptor units, and only some of these were explored in this work. The structural and chemical parameters that were varied were receptor unit, type and length of the

chain between the receptor and the thiophene (spacer), and structure of the thiophene part. The number and combination of thiophene units are relevant, though the results are not reported here. Functionalized conjugated polymers have been described in the literature. Recognition sites, such as crown ethers and calixarenes, have been covalently bound to conjugated polymers in order to obtain materials that are selective to metal ions. The behavior of the new functionalized monomers developed within this project was studied and monomers were electropolymerized, but the experimental characterization of the sensor materials is not yet complete.

Two sulfonated thiophenes, sodium 2-(3-thienyloxy)ethanesulfonate (**12**) and sodium 6-(3-thienyloxy)hexanesulfonate (**13**), were used as doping ions in the fabrication of potentiometric Ag^+ -ISEs [IV]. The thiophenes differ in the length of the alkyl chain between the charge compensator (sulfonate group) and the thiophene unit. The Ag^+ sensors were prepared by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) on glassy carbon electrodes, with either $\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$ or $\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$ as the charge compensator (doping ion) for the p-doped poly(3,4-ethylenedioxythiophene) (PEDOT). Potentiometric measurements were carried out with these sensors, glassy carbon/PEDOT($\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$) and glassy carbon/PEDOT($\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$), to evaluate their sensitivity and selectivity to silver ions. PEDOT($\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$) and PEDOT($\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$) films were also studied by techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), electrochemical quartz crystal microbalance (EQCM), and Fourier transform infrared spectroscopy (FTIR). The experimental details of these studies can be found in paper IV.

As a “soft metal”, Ag^+ interacts with the sulfur atoms of thiophene and the double bonds (π -coordination) present in the polymer backbone and the doping ion. Ag^+ -ISEs based on PEDOT doped with compounds containing sulfonate groups and/or double bonds show better sensitivity to Ag^+ than do sensors based on PEDOT doped with a weakly coordinating anion, such as hexabromocarbonane.

The potentiometric selectivity coefficients of the electrodes to Ag^+ ($\log K_{\text{Ag}^+, j}$), determined in the presence of different alkali-, alkaline-earth, and transition-metal cations, are shown in Fig. 16. The results indicate high selectivity of the glassy carbon/PEDOT($\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$) and glassy carbon/PEDOT($\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$) electrodes to Ag^+ in the presence of all the cations except Hg^{2+} , where $\log K_{\text{Ag}^+, \text{Hg}^{2+}}$ values were -0.5 for glassy carbon/PEDOT($\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$) and -0.8 for glassy carbon/PEDOT ($\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$). The selectivity coefficients were almost

identical. Results of the potentiometric measurements showed that the difference in the length of the alkyl chain of the doping ions $C_6H_7S_2O_4^-$ and $C_{10}H_{15}S_2O_4^-$ has no effect on the sensitivity and selectivity of sensors to Ag^+ . Results from cyclic voltammetry and EIS measurements, however, showed that glassy carbon/PEDOT($C_{10}H_{15}S_2O_4^-$) has higher redox capacitance and lower charge-transfer resistance than glassy carbon/PEDOT($C_6H_7S_2O_4^-$).

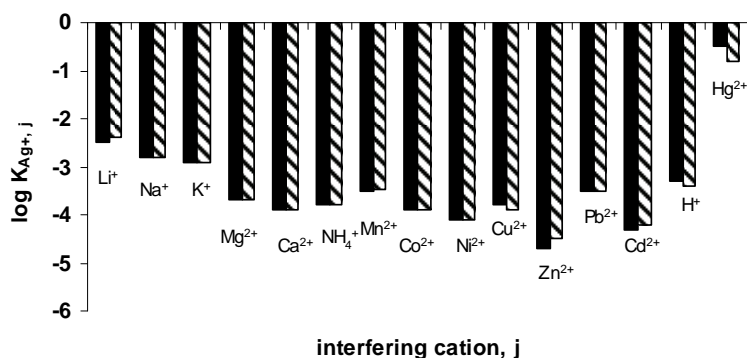


Fig. 16. Selectivity coefficients ($\log K_{Ag^+, j}$), of glassy carbon/PEDOT($C_6H_7S_2O_4^-$) (black) and glassy carbon/PEDOT($C_{10}H_{15}S_2O_4^-$) (striped) [IV].

FTIR spectra revealed nevertheless that, in the electrosynthesis of PEDOT-based films, the sulfonated thiophenes $C_6H_7S_2O_4^-$ and $C_{10}H_{15}S_2O_4^-$ are probably immobilized only as doping ions and are not covalently bound with EDOT.

Electropolymerization of azacrown ether-modified thiophene (**16**) was also performed in the presence of 3-octylthiophene. There was some indication of ion-selectivity, suggesting strong binding of Na^+ to the azacrown ether group, but the electrochemical characterization is still in progress. The developed monomers were examined systematically by cyclic voltammetry under standard conditions, but the experimental work with these sensor materials likewise is not yet complete. The new monomers that have been made available are expected to allow the preparation of sensors for several other cations and anions.

4 Conclusions

The first part of this work involved the synthesis of borate derivatives and their complexation with heteroaromatic cations and tropylium ion. In all cases, 1:1 complexes were observed by NMR spectroscopy. Potassium tetrakis(4-phenoxyphenyl)borate ($K^+\cdot\mathbf{1}$), *N*-methylpyridinium tetrakis(4-phenoxyphenyl)borate ($\mathbf{7}\cdot\mathbf{1}$), 1-ethyl-4-(methoxycarbonyl)pyridinium tetrakis(4-phenoxyphenyl)borate ($\mathbf{8}\cdot\mathbf{1}$), tropylium tetrakis(4-phenoxyphenyl)borate ($\mathbf{9}\cdot\mathbf{1}$), and imidazolium tetrakis-(biphenyl)borate ($\mathbf{10}\cdot\mathbf{3}$) were successfully crystallized and further determined by X-ray crystallography. Furthermore, the crystal structure of the alkali metal complex of tris[3-(2-pyridyl)pyrazolyl]hydroborate, i.e. potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate ($K^+\cdot\mathbf{6}$), was reported for the first time. The crystal structures showed evidence of weak noncovalent interaction. Stability constants, measured by ^1H NMR titration, were relatively low for all complexes of the borate derivatives.

The influence of borate derivatives on the selectivity and sensitivity of ion-selective electrodes was investigated by immobilizing the borate compounds as ion-recognition sites (receptors, ionophores) in potentiometric sensors for cations and metal ions. Although the use of borates in the complexation of aromatic nitrogen heterocycles has not been extensively studied, their properties suggest they are suitable for complexation of such compounds.

The second part of the work involved the synthesis and study of electropolymerized conductive polymer-based membranes containing covalently bound receptors. The chemical synthesis of functionalized monomers with covalently bound ion receptors and counterions allowed the electrosynthesis of novel conductive polymers for sensor applications. More than 15 different substituted monomers were synthesized. Since molecular recognition is based on complementarity in size, shape, and functional groups between host molecules and substrates, supramolecular chemistry can be exploited in the design and construction of ISEs for different species. Synthesis of the thiophene derivatives began with simple structures like sodium 2-(3-thienyloxy)ethanesulfonate and 2-(3-thienyloxy)ethyltriethylammonium bromide, and thereafter a number of new and tailored functionalized thiophene monomers were prepared. Several of these were successfully electropolymerized and characterized. The water-solubility of the conductive polymers with covalently bound sulfonate groups limited the applicability of some of the electropolymerized films as potentiometric cation sensors. However, the electrodes that were fabricated showed high selectivity

toward Ag^+ over several other cations. In general, the length of the alkyl chain in $\text{C}_6\text{H}_7\text{S}_2\text{O}_4\text{Na}$ and $\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4\text{Na}$ seemed to have only a minor effect on the potentiometric performance of the glassy carbon/PEDOT($\text{C}_6\text{H}_7\text{S}_2\text{O}_4^-$) and glassy carbon/PEDOT($\text{C}_{10}\text{H}_{15}\text{S}_2\text{O}_4^-$) electrodes.

Probably the most important finding of this study was that the chemical structure of aromatic borate anions plays an important role in the molecular recognition of aromatic cations. The project has generated extensive information relevant to the synthesis of borates and their interaction with cations. The results indicate that sensors for aromatic cations can be based on borate derivatives, but the selectivity also depends on the plasticizer. The project has also generated new knowledge in regard to the potentiometric sensitivities and selectivities of two types of ion sensors: solid-contact ion sensors based on plasticized PVC-based ion-selective membranes, where new insight was gained into the basic response mechanism, and conductive polymer-based membranes with electrostatically and covalently bound receptors. The experimental characterization of the new sensor materials continues.

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Original papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. Some unpublished results are included.

- I Bobacka J, Alaviuhkola T, Hietapelto V, Koskinen H, Lewenstam A, Lämsä M, Pursiainen J & Ivaska A (2002) Solid-contact ion-selective electrodes for aromatic cations based on π -coordinating soft carriers. *Talanta* 58 (2): 341–349.
- II Alaviuhkola T, Bobacka J, Nissinen M, Rissanen K, Ivaska A & Pursiainen J (2005) Synthesis, characterization, and complexation of tetraarylborates with aromatic cations and their use in chemical sensors. *Chemistry–A European Journal* 11 (7): 2071–2080.
- III Nissinen M, Alaviuhkola T, Rissanen K & Pursiainen J (2006) Crystal structure of potassium tris[3-(2-pyridyl)pyrazolyl]hydroborate. *Journal of Chemical Crystallography* 36 (12): 863–868.
- IV Mousavi Z, Alaviuhkola T, Bobacka J, Latonen R-M, Pursiainen J & Ivaska A (2007) Electrochemical characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with sulfonated thiophenes. *Electrochimica Acta*. In press.

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ISBN 978-951-42-8656-8 (Paperback)

ISBN 978-951-42-8657-5 (PDF)

ISSN 0355-3191 (Print)

ISSN 1796-220X (Online)

