**NOVEL PENTACENEDIQUINONE AND PENTACENE
DERIVATIVES**

by

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A thesis submitted to the Faculty of Graduates Studies and Research in partial fulfilment
of the requirements for the degree of Doctor of Philosophy

The Department of Chemistry

Carleton University

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the Faculty of Graduate Studies and Research
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Novel Pentacenediquinone and Pentacene Derivatives

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in partial fulfilment of the requirements
for the degree of Doctoral of Philosophy

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ABSTRACT

Pentacenediquinones are of recent interest for their rigid, linear, conjugated molecular framework. These compounds in the reduced form display absorbance in the near infrared region between 800 and 1600 nm. They are also notoriously insoluble which makes characterization very difficult.

Starting from pentacenediquinone, a series of twelve pentacenediquinones containing electron-withdrawing and electron-donating substituents were prepared.

It is hypothesized in this work, that by appropriately choosing the number, position and type of substituents, the near infrared absorbance of these compounds could be tuned and the solubility could also be improved.

Halogenated pentacenediquinones are monomers for a novel class of polymers, poly(aryl ether quinone)s. These polymers are electrochromic and display a visible colour change when being reduced. They also show a near infrared absorbance in the reduced state, between 1300 and 1400 nm for the semiquinone and between 800 and 900 nm for the dianion. Poly(aryl ether quinone)s display interesting light attenuating properties, fatigue resistance to electrochemical switching, and good adhesion to the ITO (indium-doped tin oxide) electrode. The semiquinone of poly(arylether quinone)s also displays an electrical conductivity in the order of 10^{-5} S/cm.

Halogenated pentacenediquinones can also be reduced to produce halogenated pentacenes. Four pentacenes containing halogen substituents have been prepared and their electron mobilities investigated.

In conclusion, tuning the near infrared absorbtion of pentacenediquinone through appropriate substituents has been demonstrated. The substituted pentacenediquinones are proven to be useful precursors for making a novel class of poly(aryl ether)s and substituted pentacenes.

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LIST OF EQUATIONS

Equation Description	Unit		Page
$E_{1/2} = E^{0'} + (RT/nF)\ln(D_R/D_0)^{1/2}$	(mV)	(1)	54
$E_{1/2} = E^{0'} \pm 0.001V$	(mV)	(2)	54
$\Delta E_p = E_{pa} - E_{pc} = 57/n$	(mV)	(3)	54
$\Delta E_p > 57/n$	(mV)	(4)	54
$E = hc/\lambda$	(J)	(5)	62
$E_g = E/1.6 \times 10^{-19}$	(eV)	(6)	62
$\eta_{inh} = (\ln t/t_0)/C$	(dL/g)	(7)	82
$R = U/I$	(Ω)	(8)	88
$\rho = RA/t$	(Ωcm)	(9)	88
$\sigma = 1/\rho$	(S/cm)	(10)	88
$\alpha = (\log P_0 - \log P(L))/L$	(dB/km)	(11)	89
$\text{dB}/\mu\text{m} = 10 \times (\log T_{ox} - \log T_{red})/\text{thickness}$	(dB/ μm)	(12)	89

LIST OF CONSTANTS

Constant	Description	Unit
$c = 3 \times 10^8$	Speed of light in vacuum	(m/s)
$h = 6.62 \times 10^{-34}$	Planck's constant	(Js)
$e = 1.6 \times 10^{-19}$	Elementary charge	(C)

SYMBOLS AND ABBREVIATIONS

Solvents

DMAc	<i>N,N</i> -Dimethylacetamide
DMF	<i>N,N</i> -Dimethylformamide
NMP	<i>N</i> -methyl-2-pyrrolidinone

Polymer Terminology

S _N Ar	Aromatic nucleophilic substitution
T _g	Glass transition temperature
η _{inh}	Inherent viscosity
BPA	Bisphenol A or 4,4'-(Isopropylidene)diphenol

Characterization

DSC	Differential scanning calorimetry
IR	Infrared
NIR	Near infrared
α	Optical loss (dB/km)
T _{ox}	Transmittance at the oxidation potential (dB)
T _{red}	Transmittance at the reduction potential (dB)
OTTLE cell	Optical transparent thin layer cell
E _{1/2}	Half-wave potential (mV)
E ^{0'}	Formal potential (mV)
E _{pa}	Anodic peak potential (mV)
E _{pc}	Cathodic peak potential (mV)
i _{pa}	Anodic current (μA)

i_{pc}	Cathodic current (μA)
NMR	Nuclear magnetic resonance
δ	Chemical shift (ppm)
J	Coupling constant (Hz)
mp	Melting point
MS	Mass spectrometry
HRMS	High resolution mass spectrometry
TFT	Thin film transistor
R	Electric resistance (Ω)
I	Intensity of the electric current (A)
U	Potential (V)
ρ	Resistivity (Ωm)
σ	Conductivity (S/cm)
ITO	Indium tin oxide

Chapter I. Introduction

I.1. Quinones in Nature and in the Laboratory

Quinones and semiquinones (radical anions of quinones) are quite prevalent in nature. For example, Ubiquinone Q (Figure I.1) and its corresponding semiquinone are found in virtually every living cell. As well, many aquatic species and a variety of insects use the irritating effects of quinones to protect themselves from predators. Carminic acid and juglone (Figure I.1) are quinoidal compounds responsible for some of the colours in a large variety of flowers, fruits, vegetables and insects.¹

Figure I.1. Structures of ubiquinone, juglone and carminic acid

Quinones have good thermal and light stability, and as such have been used for a long time as disperse dyes for coloring polymeric materials such as cellulose acetates, nylons and polyesters.² Over the years, some polymeric systems containing quinone units have been designed for use as redox polymers and recently as coating materials. As coating materials, the quinone-containing polymers have demonstrated their extraordinary ability to adhere to various metals and alloys with sufficient affinity to displace water from rusty surfaces.³

Among novel quinoid materials, those that contain more than one quinone moiety in their structure are becoming increasingly important.

I.2. Polyacenequinones

Polyacenequinones are aromatic compounds that contain more than one quinone moiety in their carbon framework and have up to nine rings in a row.⁴ Although the literature reports the synthesis of such linearly annulated compounds containing six to nine aromatic rings (Figure I.2), the structural proofs are considered inadequate by current standards.⁵

Figure I.2. Nonacenediquinone

The difficulty in characterization arises from the fact that these compounds are notoriously insoluble. These long, flat molecules pack very well into crystals, making purification virtually impossible and identification difficult.⁵

During the last seven years, polyacenequinones have received growing attention. Scientists began to wonder if the strong packing, electron accepting properties, and long π -conjugated framework could offer some advantages.

Recent studies done in the context of polyacenequinones show that quinoidal derivatives offer the possibility of substantially varying the electronic structure of their large molecular framework. Also, by appropriately choosing the quinone/semiquinone moiety, the optical, electrical and magnetic properties of these compounds could be controlled.⁵ The introduction of functional groups on the molecular framework would be

a solution to the solubility problem. The quinoidal groups would provide a synthetic advantage for the construction of large molecular frameworks.

As mentioned previously, quinones have long been known as electron acceptors. The radical anions of diquinones (semiquinones) behave differently from their monoquinone counterparts, displaying near-infrared absorption between 1300 and 1600 nm.⁶ This interesting property of polyacenequinones allows for new applications in the telecommunications⁷ and optical storage field⁸, shifting interest in these compounds from purely theoretical to potentially practical.

I.3 Synthesis of Polyacenequinones

In general, quinones can usually be prepared using oxidative, cyclization and annelation methods in which an additional aromatic ring is built onto an existing quinone ring.

I.3.1. Oxidative Methods

The vast majority of monoquinones are usually prepared via oxidation.⁹ The substrate is usually a phenol, phenolic ether, amine or hydrocarbon. Quinols, e.g. 1,4-hydroquinone are the easiest to oxidize when the appropriate quinol is available. In practice quinols are commonly oxidized with chromic acid or silver oxide. Although the triquinone presented in Figure I.3 can be obtained from triquinol in high yield using dichromate and sulfuric acid⁹ many quinones do not survive these harsh conditions. Thus the synthesis of large conjugated frameworks containing the quinoidal moieties must be attained using other synthetic methods.⁹

Figure I.3. Triquinone

The synthesis of polyacenequinone falls primarily into three categories: Diels-Alder cycloaddition, Aldol condensation and Friedel-Crafts acylation.

I.3.2. Diels-Alder Condensation

For the preparation of a large molecular framework, repetitive Diels-Alder cycloaddition is the method of choice.^{5,10-12} For example, Scheme I.1 shows the conversion of a monocyclic compound (benzoquinone) into a quinoidal pentacyclic product followed by a second cycle to form a tridecacyclic product.⁵ A variety of dienes can be used to react with quinones to afford the Diels-Alder adducts in various sizes, with yields usually varying between 37% and 90%.

Scheme I.1. Diels-Alder route to linear polyacenequinone derivatives

I.3.3. Aldol Condensation

Aldol condensation has also been used to prepare quinones with five, six or seven rings.^{13,14} As an example, *o*-phthalaldehyde reacts with cyclohexane-1,4-dione in a basic environment to yield a five-ring monoquinone (Scheme I.2).¹⁴ Other monoquinone derivatives were also obtained with reasonable yields between 50% and 72%.

Scheme I.2. Aldol condensation route to quinones

I.3.4. Friedel-Crafts Acylation

Another synthetic route leading to polyacenequinones is Friedel-Crafts acylation followed by cyclization.^{15,16,17} When a Lewis acid like AlCl_3 reacts with an anhydride, an acylium ion is first produced. This reactive species further reacts with an aromatic ring to produce an aryl keto-acid. Thus, condensation of pyromellitic dianhydride with benzene in the presence of aluminum chloride provides a mixture of keto-acid intermediates, which can cyclize in concentrated sulfuric acid to give pentacenediquinone (Scheme I.3).¹⁶

Scheme I.3. Friedel-Crafts acylation route to polyacenequinones

The Friedel-Crafts acylation is an important process for the manufacture of anthraquinones and is widely used in the laboratory for the preparation of polyacenequinones.¹⁵

I.4. Pentacenediquinones

Pentacenediquinones are flat, linearly annulated compounds that contain five aromatic rings and two quinone moieties. Pentacenediquinone (Figure I.4), or 5,7,12,14-pentacenetetrone (**1**) is an example of diquinone and was first prepared in 1912 by Mills and Mills using Friedel-Crafts acylation followed by cyclization in sulfuric acid. The compound appears as yellow needles, and is sparingly soluble in organic solvents.¹⁶

Figure I.4. Pentacenediquinone

Presumably due to its poor solubility, pentacenediquinone was abandoned until the early nineties. In 1989 Larry Miller and his coworkers started investigating the electrochemical behavior of pentacenediquinone among other long and short frame diquinones. This study revealed that radical anions (semiquinones) and dianions of diquinones display near-infrared (NIR) activity between 1300 and 1600 nm and respectively 880 nm.⁴ The radical anions of polyacenediquinones also show unusually high conductivity between 1 and 10^{-5} S/cm.⁶

These interesting properties led to more investigations of radical anions of polyacenequinones in order to understand their properties, NIR absorbers are of particular interest for applications in communications and optical storage.⁴ Therefore, it would be interesting to prepare a series of substituted pentacene containing electron-withdrawing (F, Cl, NO₂) and electron-donating substituents (alkyl, ether) and to investigate the NIR and electrical behaviour of the corresponding semiquinones. Figure I.5 shows a series of novel di, tetra, and hexasubstituted pentacenediquinones as potential target compounds for thesis study.

Figure I.5. Proposed mono-, di- and tri-substituted pentacenediquinones

I.5. Research Hypotheses and Directions

The chemistry of monoquinones has been well studied and reported in the literature.⁹ However, little is known about the properties, and especially NIR activity of diquinones. More investigations are needed to better understand the properties of semiquinones.

It is hypothesized in this research that the radical anions of quinones (semiquinones) offer the interesting NIR properties that could be controlled by appropriately choosing the number of substituents and their position on the external aromatic ring. It is further hypothesized that some of substituted pentacenediquinones can be used as precursors for making substituted pentacenes and pentacenediquinone-containing polymers.

It is known that some polyacenediquinones can be reduced chemically or electrochemically to the corresponding polyacenes. The chloro and fluoro groups in aromatic ketones can be readily displaced by a nucleophile such as a phenoxide.

Therefore, the thesis research can be developed into two main directions (Figure I.6). The first direction aims to study the electroactive compounds that include pentacenediquinones (small molecules) and poly(aryl ether quinone)s (polymers). The second direction investigate the semiconductive compounds like pentacene derivatives (small molecules) and the semiquinone salts of poly(aryl ether quinone)s.

Figure I.6. Research directions

Organic electronic materials tend to suffer from poor air/moisture stability and low electrical conductivity. Hence, they are of course not meant to replace the existing technology where speed and stability are crucial. However, over the years, due to assiduous research, the performance and properties of organic electronic and optoelectronic materials have considerably improved. They have recently received considerable interest for commercial applications such as displays¹⁸ and identification tags.¹⁸

This research is motivated by the interest in organic compounds that may one day find wider applications in electronics and optoelectronics. The thesis investigates the substituted pentacenediquinones and pentacenes as a class of novel compounds suitable for variable optical attenuators (optoelectronics) and organic transistors (electronics). A simple, efficient synthetic route to the substituted pentacenediquinones and pentacenes is

developed. The spectroelectrochemical and semiconductive properties of these compounds are also investigated and discussed.

The first part of the thesis (Chapters II, III, and IV) is concerned with electroactive molecules and their use as variable optical attenuators. The hypothesized statement is demonstrated, and a correlation between the molecular structure (type of substituent and position on the aromatic ring) and NIR absorbance of the semiquinone is established by spectroelectrochemical means. Also, a series of, poly(aryl ether quinone)s were prepared and studied for their electrochemical, semiconductive and optical attenuating properties.

The second part of the thesis (Chapters IV and V) presents the synthesis of some new pentacene derivatives as novel semiconductive compounds. The semiconductive properties of the small molecules and polymeric semiquinone salts were investigated using transistor templates and by two-point probe measurements.

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Chapter II. Synthesis and Characterization of Pentacenediquinones

Organic compounds, such as pentacenediquinones, to be used in the electronic and optoelectronic devices must fulfill certain requirements. First of all, the organic materials must be made inexpensive in good yields.

As presented in Chapter I, diquinones containing five to nine aromatic rings can be prepared mainly through three synthetic methods: repetitive Diels-Alder condensation, Aldol condensation and Friedel-Crafts acylation. Considering the advantages and disadvantages of these synthetic methods, it was opted for Friedel-Crafts acylation as the synthetic method for the preparation of pentacenediquinones. Friedel-Crafts acylation followed by cyclization offers the advantage of being a simple and reproducible procedure combined with high yields. A large variety of substituted benzenes commercially available can be used to prepare a series of substituted pentacenediquinones (Scheme II.1).

Scheme II.1. Synthesis of substituted pentacenediquinones

Friedel-Crafts acylation could be considered a direct method for the preparation of substituted pentacenediquinones. However, pentacenediquinones containing NO₂ and OR groups cannot be obtained directly as products of acylation. Therefore, indirect synthetic methods like nitration and halide displacement should be used for the introduction of such functional groups.

II.1. Friedel-Crafts Acylation

In the past, the Friedel-Crafts acylation has been regarded more as a branch of the related alkylation reaction rather than a separate topic. The fundamental difference between these two, namely the amount of catalyst required, has been always recognized but largely ignored.¹

The term “acylation” is interpreted as the direct formation of compounds containing a carbonyl group attached to the aromatic system.¹ This definition includes the formation of ketones, carboxaldehydes and carboxylic acids but does not include the related Gattermann aldehyde synthesis or the Houben-Hoesch ketone synthesis.¹

In general, Friedel-Crafts acylation involves three reactants: a hydrocarbon (benzene or substituted benzene), an acyl component and a catalyst (Lewis acid).² The acyl component in the acylation can be any substance which, under the influence of the catalyst, will give rise to a potential acyl cation. Usually, for the introduction of an acyl group (RCO-) onto an aromatic nucleus, acid chlorides are frequently used. Carboxylic acids, esters and anhydrides can also be used in the acylation.³ In the case of pentacenediquinones, various substituted benzenes are used as aromatic hydrocarbons and pyromellitic tetracarboxylic dianhydride is used as the acyl component. Aluminum

chloride is most generally used as a catalyst since it is the least expensive and the most efficient catalyst in this reaction.

Anhydrous conditions are an absolute requirement for Friedel-Crafts acylation. However, in practice, absolute anhydrous conditions are very difficult to obtain. Some research groups have claimed that very small amounts of water added to anhydrous aluminum chloride caused considerable improvements in yield.⁶

In order to obtain good yields, stoichiometric amounts of aluminum chloride are required for complete consumption of the acyl component. Many poor yields have been attributed to insufficient amounts of catalyst used. The direct relationship between acyl component and catalyst can be illustrated as follows (Scheme II.2):

Scheme II.2. Schematic utilization of the catalyst

The optimum ratio of the number of moles catalyst to the number of moles of acyl component has been determined to be 3 for equation (2).⁷

Monosubstituted benzene derivatives are acylated predominantly in the *para* position, which has been attributed to an attacking reagent of large steric requirements.⁸ The acylation mechanism occurs through the attack of a π bond of the benzene ring to the acylium ion formed in the reaction between the anhydride and the Lewis acid (Scheme II.3).³

Scheme II.3. Friedel-Crafts acylation mechanism

The carbonyl group in the ketone product is positively polarized and is attached directly to the aromatic ring. The ketone product is deactivated relative to the starting material, therefore further reaction to give a polyacylated derivative is not a problem since the acylium ion is less reactive than benzene. Acylium ions are resonance stabilized and are not subject to skeletal rearrangement prior to reaction with the aromatic ring.³

II.1.1. Aromatic Hydrocarbon

In the acylation of aromatic hydrocarbons it is generally difficult to introduce more than one acyl group into the nucleus. The acyl group first introduced is present in the reaction media as an aluminum chloride complex, which produces a powerful deactivating complex on any subsequent electrophilic acylation.⁶ Friedel-Crafts acylation proceeds successfully not only with aromatic hydrocarbons, but also with some of their substituted derivatives like halogeno-, alkoxy- and amino- derivatives. It has been observed that if an electronegative group is present in the hydrocarbon, it will have an inhibiting effect on the reaction. This phenomenon is mostly observed with monocyclic aromatics; for example, nitrobenzene, benzoic acid and benzophenone are very difficult to acylate.

It is not possible to obtain the precursor for dinitropentacenediquinone using acylation as a synthetic method. Such a substituent must be introduced through an indirect synthetic procedure that will be presented in a future chapter.

Halogens attached to the aromatic ring exert a retarding influence on the rate of substitution. The intensity of the effect increases with the number of halogen atoms present on the ring, but is not prohibitive.⁶ It is therefore possible to prepare substituted pentacenediquinones containing a various number of halogens on the external aromatic rings starting from substituted benzenes. The results for the acylation of pyromellitic dianhydride with various benzenes are presented in Table II.1.

Table II.1. Acylation results and conditions

Compound	Benzene type	Acylation conditions	Yield (%)
1		Reflux 4 hours at 80 °C	57
2a and 2b		Reflux 4 hours at 85 °C	81
3		Reflux 4 hours at 89 °C	50
6a and 6b		Reflux 4 hours at 132 °C	80
7a and 7b		Reflux 4 hours at 173 °C	78
8a, 8b and 8c		Reflux 4 hours at 180 °C	42
9a and 9b		Reflux 4 hours at 214 °C	60
10		Reflux 4 hours at 90 °C	93

II.2. Cyclization

As presented in Chapter I.1.4.4., unsubstituted pentacenediquinone is prepared in two steps, Friedel-Crafts acylation followed by cyclization in an acidic environment (Figure I.6.). The cyclization is usually carried out by heating in sulphuric acid, or occasionally in polyphosphoric acid.⁹ The cyclization *ortho* to a carbonyl group proceeds with good efficiency. Unsubstituted pentacenediquinone is obtained by the action of concentrated sulphuric acid on the ketoacids mixture (Scheme II.4.).

Scheme II.4. Synthesis of pentacenediquinone **1**

However, the substitution pattern may play a considerable role in this step. Cyclization is very difficult when two *ortho/para* directing substituents are located *meta* to the site of cyclization (Figure II.1.).⁹

Figure II.1. Ketoacids containing *ortho* and *para* directing substituents *meta* to the cyclization position

In the case of a strong acid like H_2SO_4 and at high temperatures, the cyclization of halogenated ketoacids occurs either with the formation of a lactone (for the hexachloro substituted ketoacid), or as a reaction of isomerization (Scheme II.5).⁹

Scheme II.5. Cyclization in sulphuric acid for substituted ketoacids

The mechanism presented in Scheme II.5. provides a good explanation for the failure of cyclization of ketoacids containing *ortho* and *para* directing substituents located *meta* to the position of cyclization using sulphuric acid. For the preparation of substituted pentacenediquinones from the corresponding ketoacids various other methods were tried; cyclization in sulphuric acid and boiling benzoyl chloride; cyclization in sulphuric acid and boric acid; conversion of the carboxylic acid into the corresponding

acid chloride followed Friedel-Crafts acylation in nitrobenzene or dichloromethane using aluminum chloride or zinc chloride as a catalyst (Scheme II.6).^{10,11}

Scheme II.6. Trials for the preparation of substituted pentacenediquinones

Unfortunately, all these methods failed to produce the substituted pentacenediquinones. Therefore, for the closing of substituted ketoacids, a more vigorous procedure would be needed in order to overcome the orientation effects of the substituents.

Friedel-Crafts acylation using AlCl_3 melt¹² in the presence of NaCl is the only method that produced the desired pentacenediquinones (Scheme II.7). However, for this type of acylation a very large amount of aluminum chloride is needed, usually 7 grams per gram ketoacid. High temperature (180°C) is also required for the melting of aluminum chloride, and the reaction time is four hours. The yield varies between 40 and 65%, and the products can be purified through vapour train sublimation.

Scheme II.7. Friedel-Crafts cyclization in aluminum chloride melt

The results for the cyclization of ketoacids are presented in Table II.2.

Table II.2. Cyclization of ketoacids

Compound	Cyclization conditions	Yield (%)
1	H ₂ SO ₄ , heating at 100 °C for 5 hours	95
2a and 2b	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	47
3	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	46
6	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	36
7a and 7b	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	9.6
8a, 8b and 8c	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	23
9a and 9b	Al ₂ Cl ₃ melt, heating at 200 °C for 4 hours	23
10	H ₂ SO ₄ , heating at 100 °C for 5 hours	69

Substituted pentacenediquinones are usually obtained as mixtures of two isomers. For some applications, the presence of another isomer does not affect the overall performance, but in most cases a material of very high purity is required.

II.3. Separation of Isomers

As it was mentioned previously, the substituted pentacene-diquinones are obtained as mixtures of isomers. Some applications require the organic material to be of very high purity. This is especially true for organic transistors, where good charge

mobility is a prerequisite. The presence of another isomer may affect the molecular packing, acting like a trap and lowering the mobility of the material.

A very simple method for the separation of isomers was designed. First, the isomeric ketoacid mixture was transformed into a mixture of esters¹³ in the presence of anhydrous ethanol and sulphuric acid as the catalyst (Scheme II.8). The esterification was allowed to proceed for 48 hours and produced a mixture of two isomers. One is insoluble and crystalline and precipitates out of solution (**2''a** respectively **6''a**), while the other one is amorphous and remains in solution (**2''b** respectively **6''b**).

Scheme II.8. Separation of the two isomeric **2'a, b** and **6'a, b**

The structure of both isomers can be ascertained by nuclear magnetic resonance (NMR) spectroscopy (Figure II.2).

Figure II.2. ^1H NMR (400 MHz) spectrum of the two isomeric esters **6''a** in DMSO- d_6 and **6''b** in CDCl_3

The ^1H NMR spectrum of both isomers **6''a** and **6''b** exhibit the expected splitting patterns. The structural differences are illustrated by the protons from the middle aromatic ring. For isomer **6''a** just one signal is visible at 8.1 ppm as a singlet, while for isomer **6''b** two signals are visible at 8.7 and 7.4 ppm as singlets.

The esters are cleaved to the corresponding ketoacids using a solution of 48% aqueous HBr in acetic acid as the solvent.¹⁴ The reaction requires 48 hours of reflux and usually proceeds with 97% yield. The ester separation results and ^1H NMR assignments are presented in Table II.3.

Table II.3. ^1H NMR proton assignments for the F- and Cl-esters and the corresponding ketoacids

Compound	Yield (%)	m.p. (°C)	^1H NMR proton assignment
2''a	65	238 - 242	δ (ppm): 8.0 (s, 1 H_a), 7.83 (dd, $J_1 = 5.3$ Hz, $J_2 = 3.2$ Hz, 2 H_b), 7.18 (t, $J = 8$ Hz, 2 H_c), 4.17 (q, $J = 8$ Hz, CH_2) 1.12 (t, $J = 8$ Hz, CH_3)
2''b	35	90 - 100	δ (ppm): 8.55 (s, 1 H_a), 7.81 (dd, $J_1 = 5.6$ Hz, $J_2 = 3.2$ Hz, 2 H_c), 7.72 (s, 1 H_b), 7.36 (t, $J = 8.8$ Hz, 2 H_d), 4.13 (q, $J = 8$ Hz, CH_2), 1.05 (t, $J = 8$ Hz, CH_3)
6''a	56	232	δ (ppm): 8.06 (s, 1 H_a), 7.8 (d, $J = 12$ Hz, 2 H_b), 7.63 (d, $J = 8$ Hz, 2 H_c), 4.07 (q, $J = 8$ Hz, CH_2), 1.03 (t, $J = 8$ Hz, CH_3)
6''b	46	120	δ (ppm): 8.76 (s, 1 H_a), 7.70 (d, $J = 8$ Hz, 2 H_c), 7.45 (d, $J = 8$ Hz, 2 H_d), 7.35 (s, 1 H_b), 4.14 (q, $J = 8$ Hz, CH_2), 1.09 (t, $J = 8$ Hz, CH_3)
2'a	89	309	δ (ppm): 13.7 COOH, 7.95 (s, 1 H_a), 7.84 (dd, $J_1 = 5.6$ Hz, $J_2 = 3.2$ Hz, 2 H_b), 7.37 (t, $J = 8.8$ Hz, 2 H_c)
2'b	80	230	δ (ppm): 13.7 COOH, 8.56 (s, 1 H_a), 7.81 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 2 H_c), 7.57 (s, 1 H_b), 7.34 (t, $J = 8$ Hz, 2 H_d)
6'a	70	321	δ (ppm): 13.8 COOH, 7.95 (s, 1 H_a), 7.75 (d, $J = 8$ Hz, 2 H_b), 7.59 (d, $J = 8$ Hz, 2 H_c)
6'b	80	264	δ (ppm): 13.8 COOH, 8.55 (s, 1 H_a), 7.7 (d, $J = 8$ Hz, 2 H_c), 7.6 (d, $J = 8$ Hz, 2 H_d), 7.5 (s, 1 H_b)

The ketoacids can be cyclized to produce the corresponding pentacenediquinone using the AlCl_3 melt procedure.

II.4. Introduction of Nitro Groups

Pentacenediquinone **1** is relatively unreactive towards electrophilic aromatic substitution due to the presence of four carbonyl groups. The carbonyl groups have a strong deactivating effect on the two external aromatic rings. The nitration of pentacenediquinone **1** proceeds smoothly to yield two isomeric dinitropentacenediquinones that were difficult to separate (Scheme II.9.).

Thus pentacenediquinone was dissolved in concentrated sulphuric acid, and a nitrating mixture consisting of equal amounts of fuming nitric acid and sulphuric acid was slowly added to the solution.¹⁵ After addition of the nitrating mixture, the solution was gently heated. The reaction was usually allowed to proceed for four hours. Yields varied between 65 and 90%.

Scheme II.9. Nitration of pentacenediquinones

Difluoropentacenediquinones **2a** and **2b** were also nitrated with similar yields producing the two isomers (Scheme II.9.) The nitration results are presented in Table II.4.

Table II.4. Nitration results

Compound	Starting material	Reaction conditions	Yield (%)	m.p. (°C)
4a, 4b	2a, 2b	4 hours at 65 °C	83	247 – 270 decomposition
5a, 5b	1	4 hours at 65 °C	89	215 – 245 decompositon

II.5. Introduction of Ether Groups

Ether groups can be introduced using a classic halide displacement reaction.¹⁶ Phenols can displace the halide in the presence of a weak base like K_2CO_3 . The displacement of fluoride occurs with ease and therefore the fluorinated pentacenediquinones are preferred for the preparation of aryl ether pentacenediquinones over their chlorinated counterparts.

Scheme II.10. Introduction of ether groups

Tert-butylphenol was used as the corresponding phenol for the displacement of the halide in an attempt to impart solubility to the products **11a**, **b** and **12**. Yields for all the displacement reactions were 70-97% (Table II.5).

Table II.5. Preparation of aryl ether pentacenediquinone

Compound	Starting material	Reaction conditions	Yield (%)
11a and 11b	2a and 2b	Reflux at 154 °C for 24 hours	90
11a	2a	Reflux at 154 °C for 24 hours	92
11b	2b	Reflux at 154 °C for 24 hours	97
12	3	Reflux at 154 °C for 24 hours	69

II.6. Characterization of Pentacenediquinones

Characterization of substituted pentacenediquinone was carried out using traditional methods, such as mass spectroscopy (MS), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) when solubility allowed.

II.6.1. Mass Spectrometry

Due to their poor solubility, pentacenediquinones are characterized mostly through mass spectrometry. Mass spectrometry is widely used in the field of natural compounds for the characterization of naturally occurring quinones, due to the advantage

that minute amounts of substance are sufficient for identification and structure elucidation.

A general observation in the case of all 1,4-quinones is the formation of an M+2 peak. The appearance of this peak is due to the partial reduction of quinones by the residual moisture present in the inlet system and ionization chamber.¹⁷ In a similar way to monoquinones (benzoquinones, naphthoquinones), diquinones show a gradual loss of four CO molecules. For example, the mass spectra of pentacenediquinone 1 presents the usual loss of C=O and the characteristic [M+2] peak. The molecular ion peak appears at 338 *m/e*, and the gradual loss of C=O can be observed at 310, 282, 254 and 226 *m/e* (Figure II.3).

Figure II.3. EI mass spectra of pentacenediquinone 1

In the case of chlorine substituents, the M+2 peak becomes very significant. The heavy isotope of Cl is two mass units heavier than the lighter isotope, and the natural abundance of ^{37}Cl is 32.5% that of ^{35}Cl . Therefore, the intensity of the M+2 peak in a compound containing one chlorine atom should be 32.5% of the intensity of the molecular ion peak. When two chlorine atoms are present, a very distinct M+4 peak, and a very intense M+2 peak should be observed.¹⁸ In the case of dichloropentacenediquinone (Figure II.4.), the presence of a M+2 peak of roughly 60% of the intensity of the molecular ion peak can be observed. Chlorine patterns can be observed for all pentacenediquinones that contain more than one chlorine atom, such as tetrachloropentacenediquinones and hexachloropentacenediquinones.

Figure II.4. EI mass spectra of dichloropentacenediquinone 6a

The molecular ion peaks for the pentacenediquinone series are presented in Table II.6.

Table II.6. Molecular ion peaks for pentacenediquinones

Compound	Molecular formula	HRMS molecular ion peak
1	C ₂₂ H ₁₀ O ₄	338.0579 calcd., 338.0598 found
2a and 2b	C ₂₂ H ₈ F ₂ O ₄	374.0390 calcd., 374.0379 found
3	C ₂₂ H ₆ F ₄ O ₄	410.0202 calcd., 410.0180 found
4a and 4b	C ₂₂ H ₆ F ₂ N ₂ O ₈	464 (MS m/e 100)
5a and 5b	C ₂₂ H ₈ N ₂ O ₈	428.0280 calcd., 428.0298 found
6a and 6b	C ₂₂ H ₈ Cl ₂ O ₄	405.9799 calcd., 405.9812 found
7a and 7b	C ₂₂ H ₆ Cl ₄ O ₄	473.9020 calcd., 473.8991 found
8a, 6b and 8c	C ₂₂ H ₆ Cl ₄ O ₄	473.9020 calcd., 473.8991 found
9a and 9b	C ₂₂ H ₄ Cl ₆ O ₄	541.8201 calcd., 541.8243 found
10	C ₂₆ H ₁₈ O ₄	394.1205 calcd., 394.1209 found
11a and 11b	C ₄₂ H ₃₄ O ₆	634.2355 calcd., 634.2360 found

II.6.2. Infrared Spectroscopy

Infrared spectroscopy is a very important tool for the characterization of pentacenediquinones. From the infrared spectrum the strong absorption that corresponds to the C=O peak at 1680 cm⁻¹ shifted at lower frequency due to the conjugation with an aromatic ring, and a peak at 1587 cm⁻¹ that corresponds to the C=C aromatic bond can also be observed.¹⁹ The presence of these two peaks can be observed for all quinones, and their positions may be slightly dependent on the substitution pattern.

The first compound of the pentacenediquinone series, pentacenediquinone crystallizes as yellow needles and is sparingly soluble in organic solvents. The melting point reported in the literature after recrystallization from hot nitrobenzene is 408 °C.²⁰ The infrared spectra of pentacenediquinone presents the two characteristic peaks observed for all pentacenediquinones: at 1680 cm⁻¹ for the C=O group and at 1587 cm⁻¹ for the C=C aromatic bonds (Figure II.5.).

Figure II.5. Infrared spectrum of unsubstituted pentacenediquinone 1

The characteristic IR peaks for all pentacenediquinones are presented in Table II.7.

Table II.7. Characteristic IR peaks for pentacenediquinones

Compound	Characteristic IR peaks [cm^{-1}]
1	1673 (C=O carbonyl), 1592 (C=C aromatic)
2a and 2b	1682 (C=O carbonyl), 1587 (C=C aromatic)
3	1681 (C=O carbonyl), 1583 (C=C aromatic)
4a and 4b	1684 (C=O carbonyl), 1600 (C=C aromatic), 1555 and 1485 (NO_2)
5a and 5b	1683 (C=O carbonyl), 1592 (C=C aromatic), 1538 and 1480 (NO_2)
6a and 6b	1683 (C=O carbonyl), 1587 (C=C aromatic)
7a and 7b	1681 (C=O carbonyl), 1569 (C=C aromatic)
8a, 8b and 8c	1680 (C=O carbonyl), 1577 (C=C aromatic)
9a and 9b	1681 (C=O carbonyl), 1548 (C=C aromatic)
10	1667 (C=O carbonyl), 1541 (C=C aromatic)
11a and 11b	1677 (C=O carbonyl), 1589 (C=C aromatic), 1274-1170 (C-O ether)
12	1677 (C=O carbonyl), 1590 (C=C aromatic), 1322-1002 (C-O ether)

In the case of compounds **3**, **7**, **8** and **9**, the presence of a halogen atom on the α carbon shifts the carbonyl absorption peak to a higher frequency (Table II.7). The electron-withdrawing effect removes electrons from the carbon of the C=O bond. This removal is compensated for by a thickening of the π bond (shortening), which increases

the force constant and leads to an increase in the absorption frequency.¹⁹ The same effect can be observed also in the case of compounds **4** and **5** when the NO₂ group is present on the aromatic ring. Substituents like CH₃ and ether groups have the opposite effect, shifting the carbonyl absorption peak to a lower frequency (e.g. compounds **10**, **11** and **12**).

II.6.3. Nuclear Magnetic Resonance Spectroscopy

Due to the poor solubility of pentacenediquinone **1** there are no NMR spectra reported in the literature. A ¹H NMR spectrum in DMSO-d₆ was recorded, and it is probably the only one reported up to date.

Figure II.6. ¹H NMR (400 MHz) spectrum of pentacenediquinone **1** in DMSO-d₆

The splitting pattern appears as expected, H_a from the benzene middle ring is present at 8.89 ppm as a singlet, H_b from the external aromatic ring appears as a doublet of doublet at 8.30 ppm and finally H_c appears as a doublet of doublets at 8.01 ppm. ¹H NMR spectra were also obtained for compounds **3** and **11a**. The proton assignments are presented in Figure II.7 and Table II.8.

Figure II.7. Proton assignments for compounds **3** and **11a****Table II.8.** ^1H NMR chemical shifts, proton assignments and coupling constants for compounds **1**, **3** and **11a**

Compound	^1H NMR chemical shifts, proton assignments (δ ppm) and coupling constants (J Hz)
1	8.89 (s, 1 H_a), 8.30 (dd, $J_1 = 5.6$ Hz, $J_2 = 2$ Hz, 1 H_b), 8.0 (dd, $J_1 = 5.6$ Hz, $J_2 = 2.8$ Hz, 1 H_c),
3	8.7 (s, 1 H_a), 7.80 (dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1 H_b)
11a	9.09 (s, 1 H_a), 8.27 (dd, $J_1 = 8.8$ Hz, $J_2 = 2$ Hz, 1 H_c), 7.73 (s, 1 H_b), 7.39 (d, $J = 10$ Hz, 1 H_e), 7.33 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1 H_d), 6.98 (d, $J = 10$ Hz, 1 H_f), 1.3 (s, 9H, CH_3)

For compound **3** only two signals are visible on the NMR spectrum due to the symmetry of the molecule. The signal from the middle aromatic ring (H_a) is visible as a singlet at 8.89 ppm, and proton H_b in the vicinity of the fluorine atom appears as a doublet of doublets at 7.80 ppm. For compound **11a** the proton from the middle aromatic ring (H_a) is visible as a singlet at 9.09 ppm. Proton H_b from the external aromatic ring appears as a singlet at 7.73 ppm and protons H_c and H_d are also visible as doublets of doublets at 8.27 and respectively 7.33. Protons H_e and H_f belonging to the aromatic ring from the ether linkage are visible as doublets at 7.39 and 6.98 ppm.

II.7. Conclusion

A series of twelve substituted pentacenediquinones were prepared using Friedel-Crafts acylation followed by cyclization in aluminum chloride melt. Attempts to

solubilize these compounds were made by introducing nitro- and bulky ether groups. Isomeric pentacenediquinones were also obtained after the separation of the ketoacids using Fisher esterification followed by the cleavage of the corresponding ester in an acidic environment. The novel series of pentacenediquinones were characterized using conventional methods: mass spectrometry, infrared spectroscopy and nuclear magnetic resonance spectroscopy.

II.8. Experimental Procedure

General Methods

Infrared spectra were recorded on a Bomem Michelson 120 Fourier transform instrument. ^1H NMR and ^{13}C NMR spectra were measured using a Bruker-400 (400 MHz) and Varian (100 MHz) FT-NMR spectrophotometer, respectively. Melting points were determined on a Fisher-Johnes melting point apparatus and a Seiko DSC 220 at a heating rate of 10 °C per minute under nitrogen. Mass spectral analysis was performed at the University of Ottawa Mass Spectrometry Centre using a Kratos Concept 1H mass spectrometer. Pentacenediquinones have been prepared as mixtures of isomers and also as pure isomers. All pentacenediquinones, with exception of diether and tetraether tertbutylphenyl pentacenediquinone (compounds **11 a**, **b** and **12**), have been purified by sublimation at 450 °C at 10^{-5} mmHg.

Materials

Chemicals were purchased from Aldrich, with exception of AlCl_3 that was obtained from Fluka. All the halogenated benzenes (mono-, di-, and tri-substituted) were dried over P_2O_5 and freshly distilled over molecular sieves. Anhydrous benzene was

stored over molecular sieves. K_2CO_3 was ground and dried in an oven at 200 °C for 24 hours prior to use.

Pentacenediquinone (1)

Pyromellitic dianhydride (1.000g, 0.0045 mol) was placed into a flame dried flask equipped with a magnetic stirrer and a reflux condenser. To the flask were added 20 mL of anhydrous benzene and AlCl_3 (2.4g, 0.018 mol). Upon heating the mixture turned a bright yellow color. The suspension was heated to reflux for four hours. The excess benzene was distilled off and the obtained residue was carefully decomposed on ice and HCl. The chunky solid was filtered and dissolved in a solution of NaHCO_3 . The resulting solution was filtered to remove eventual insoluble inorganic solids, and the clear liquid was acidified with concentrated HCl. Upon acidification a white precipitate was obtained. The solid was isolated through suction filtration, dried in a vacuum oven overnight at 100 °C to yield 0.978g (57 %) white solid. The white solid (0.978g, 0.0026 mol) and 8 mL concentrated sulphuric acid were placed in a flame-dried flask equipped with a magnetic stirrer and fitted with an air condenser. The resulting brown yellowish solution was heated on an oil bath at 120 °C for five hours. Upon cooling a large mass of fine yellow needles precipitated. The suspension was carefully poured on ice, and the needle like precipitate was removed by suction filtration over a frit. The precipitate was then stirred in a saturated NaHCO_3 solution to remove the unreacted acid, filtered and then stirred

again in acetic acid. Finally, the compound was filtered, dried shortly in a vacuum oven at 120 °C and recrystallized from nitrobenzene. After recrystallization and drying in a vacuum oven at 220 °C for 24 hours, 0.841g (95 %) of golden needles were obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1673 (C=O carbonyl), 1592 (C=C aromatic), 1310, 1266, 1128, 969, 704. ^1H NMR (DMSO- d_6): δ 8.89 (s, 1H), 8.30 (dd, $J_1 = 5.6$ Hz, $J_2 = 2$ Hz, 1H), 8.0 (dd, $J_1 = 5.6$ Hz, $J_2 = 2.8$ Hz, 1H). HRMS calcd. for $\text{C}_{22}\text{H}_{10}\text{O}_4$: 338.0579, found: 338.0598.

General procedure for the cyclization in AlCl_3 melt

The ketoacids mixture (1.000g) was placed in a mortar and ground together with 7.000g of AlCl_3 and 1.000g NaCl until a homogenous fine powder was obtained. The powder was introduced into a flame dried round bottom flask that was fitted with an air condenser. The mixture was heated at 200 °C for 4 hours. Upon heating, the melt usually takes a purple color. After 4 hours, the melt was allowed to cool to room temperature and a mixture of ice and HCl was carefully added to the flask. The solid was allowed to decompose overnight. The colored precipitate was isolated by suction filtration and stirred for four hours in a saturated NaHCO_3 solution to remove the unreacted acid. The precipitate was then filtered and finally stirred in acetic acid. After filtration, the product was dried in a vacuum oven at 200 °C for 24 hours. The yield usually varied between 45 and 65%.

2,9-; 2,10-Difluororopentacenediquinone (2)

Starting with 4.000g (0.018 mol) pyromellitic dianhydride and 30 mL fluorobenzene, the ketoacids mixture was prepared following the procedure outlined for the synthesis of compound **1**. A white precipitate (6.000g) was obtained with a 81 % yield. The ketoacid mixture (1.000g) was then cyclized using the general cyclization procedure in AlCl_3 . After recrystallization from hot nitrobenzene and sublimation at 450°C and 10^{-5} torr, 0.430 g (47 %) of a yellow precipitate was obtained. m.p. $> 400^\circ\text{C}$; IR (KBr cm^{-1}): 1682 (C=O carbonyl), 1587 (C=C aromatic), 1472, 1401, 1277, 1090, 994, 943, 849, 714, 690, 639. HRMS calcd. for $\text{C}_{22}\text{H}_8\text{F}_2\text{O}_4$: 374.0390, found 374.0379.

Difluoroketoesters (2''a and 2''b)

Anhydrous ethanol (50 mL) and a mixture of 5.000 g (0.011 mol) isomeric ketoacids (**2' a, b**) are introduced in a flame dried flask equipped with magnetic stirrer and reflux condenser. To the suspension was added 1 mL of concentrated H_2SO_4 as a catalyst. The reaction mixture was heated to reflux for 48 hours. The suspension was allowed to cool to room temperature and a white crystalline solid precipitated at the bottom of the flask. The solid was removed through suction filtration. After stirring in a

solution of 20% NaHCO_3 , acetone, and recrystallization from toluene, 3.600 g (65 %) of the pure ester **2''a** was obtained as white prisms. The ethanolic solution containing the other isomer was concentrated in vacuum and the yellow residue taken in chloroform. The organic layer is washed with a solution 20 % K_2CO_3 until no longer acidic. The chloroform solution was dried over anhydrous MgSO_4 and the solvent removed in vacuo. Ester **2''b** was obtained as an amorphous white-yellowish solid (2.000 g, 35 %).

Difluoroketoester (**2''a**)

m.p.= 238 - 242 °C; IR (KBr cm^{-1}): 1721 ($\text{C}=\text{O}$ ester), 1682 ($\text{C}=\text{O}$ carbonyl), 1597 ($\text{C}=\text{C}$ aromatic), 1503, 1410, 1374 – 1016 ($\text{C}-\text{O}$ ester), 949, 921, 845, 749. ^1H NMR (CDCl_3): δ 8.0 (s, 1H), 7.83 (dd, $J_1 = 5.3$ Hz, $J_2 = 3.2$ Hz, 2H), 7.18 (t, $J = 8$ Hz, 2H), 4.17 (q, $J = 8$ Hz, 2H), 1.12 (t, $J = 8$ Hz, 3 H). ^{13}C NMR (CDCl_3): δ 193.8, 167.3 ($^1J_{\text{C-F}} = 254$ Hz), 164.2, 142.4, 132.9 ($^4J_{\text{C-F}} = 3$ Hz), 132.5, 132.1 ($^3J_{\text{C-F}} = 9$ Hz), 129.6, 116.0 ($^2J_{\text{C-F}} = 22$ Hz), 62.3, 13.6. HRMS calcd. for $\text{C}_{22}\text{H}_{30}\text{F}_2\text{O}_6$: 466.1273, found 466.1233.

Difluoroketoester (**2''b**)

m.p.= 90 - 100 °C; IR (KBr cm^{-1}): 1727 ($\text{C}=\text{O}$ ester), 1680 ($\text{C}=\text{O}$ carbonyl), 1597 ($\text{C}=\text{C}$ aromatic), 1506, 1410, 1301 – 1042 ($\text{C}-\text{O}$ ester), 921, 853, 751. ^1H NMR ($\text{DMSO}-d_6$): δ

8.55 (s, 1H), 7.81 (dd, $J_1 = 5.6$ Hz, $J_2 = 3.2$ Hz, 2H), 7.72 (s, 1H), 7.36 (t, $J = 8.8$ Hz, 2H), 4.13 (q, $J = 8$ Hz, 2H), 1.05 (t, $J = 8$ Hz, 3 H). ^{13}C NMR (DMSO- d_6): δ 193.6, 166.4 ($^1J_{\text{C-F}} = 254$ Hz), 163.9, 144.4, 132.7 ($^4J_{\text{C-F}} = 3$ Hz), 132.0 ($^3J_{\text{C-F}} = 9.6$ Hz), 131.2, 129.6, 126.9, 115.9 ($^2J_{\text{C-F}} = 22$ Hz), 61.8, 13.3. HRMS calcd. for: $\text{C}_{22}\text{H}_{30}\text{F}_2\text{O}_6$: 466.1273, found 466.1233.

Difluoroketoacid (2'a)

In a 100 mL round bottomed flask equipped with magnetic stirring were added 3.000 g (0.005 mol) of ester **2''a**, 50 mL of glacial acetic acid and 5 mL of 48% aq. HBr. The flask was then fitted with a reflux condenser and the mixture heated at 120 °C for 48 hours. The suspension was allowed to cool to room temperature, and then 10 mL of cold distilled H_2O was added to the mixture. The flask was kept on ice for two hours. The white solid was filtered by suction and the compound dissolved in a saturated NaHCO_3 solution. The resulting solution was filtered to remove the unreacted ester and the clear liquid was acidified with HCl until pH = 1. The white precipitate was filtered over a frit and dried under vacuum at 100 °C for 24 hours affording 2.000 g (89 %) of the corresponding acid. m.p.= 309 °C; IR (KBr cm^{-1}): 3500 – 3000 (OH carboxylic acid), 1701 (C=O carboxylic acid), 1678 (C=O carbonyl), 1596 (C=C aromatic), 1526, 1412, 1269 – 1013 (C-O carboxylic acid), 922, 782. ^1H NMR (DMSO- d_6): δ 13.7 (s, 1H), 7.95 (s, 1H), 7.84 (dd, $J_1 = 5.6$ Hz, $J_2 = 3.2$ Hz, 2H), 7.37 (t, $J = 8.8$ Hz, 2H). ^{13}C NMR

(DMSO- d_6): δ 193.6, 166.3 ($^1J_{C-F}$ = 252 Hz), 165.6, 141.8, 133.2, 133.0, 132.1 ($^3J_{C-F}$ = 9 Hz), 128.7, 115.9 ($^2J_{C-F}$ = 22 Hz). HRMS calcd. for $C_{22}H_{12}F_2O_6$: 410.0612, found 410.0608.

2,9-Difluoropentacenediquinone (2a)

Starting with the acid **2'a** (2.000g) and following the general procedure for the cyclization in $AlCl_3$ melt, 1.400g of **2a** were obtained with 77 % yield. The quinone was recrystallized from hot nitrobenzene producing 1.200g of golden prisms of **2a**. mp > 400 °C; IR (KBr cm^{-1}): 1678 (C=O carbonyl), 1587 (C=C aromatic), 1468, 1265, 1216, 946, 851, 721. HRMS calcd. for $C_{22}H_8F_2O_4$: 374.0390, found 374.0379.

Difluoroketoacid (2'b)

Compound **2'b** was prepared using the same procedure as for **2'a**. **2'b**: 1.407 g (80%), m.p.= 230 °C; IR (KBr cm^{-1}): 3500 – 3000 (OH carboxylic acid), 1705 (C=O carboxylic acid), 1675 (C=O carbonyl), 1596 (C=C aromatic), 1506, 1412, 1269 – 1113 (C-O carboxylic acid), 922, 782. 1H NMR (DMSO- d_6): δ 13.7 (s, 1H), 8.56 (s, 1H), 7.81 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.57 (s, 1H), 7.34 (t, J = 12 Hz, 2H). ^{13}C NMR (DMSO-

d_6): δ 193.6, 166.2 ($^1J_{C-F} = 251$ Hz), 165.7, 144.6, 133.0, 131.8 ($^3J_{C-F} = 10$ Hz), 131.4, 130.6, 126.4, 115.8 ($^2J_{C-F} = 22$ Hz). HRMS calcd. for $C_{22}H_{12}F_2O_6$: 410.0612, found 410.0608.

2,10-Difluoropentacenediquinone (2b)

Starting with the acid **2'b** (1.500g) and following the general procedure for the cyclization in $AlCl_3$ melt, 0.800g of **2b** was obtained in 60% yield. The quinone was recrystallized from hot nitrobenzene producing 0.78g golden prisms of **2b**. m.p. > 400 °C, IR (KBr cm^{-1}): 1674 (C=O carbonyl), 1581 (C=C aromatic), 1468, 1275, 1126, 946, 851, 721. HRMS calcd. for $C_{22}H_8F_2O_4$: 374.0390, found 374.0379.

1,4,8,11-Tetrafluoropentacenediquinone (3)

Starting with 2.000g (0.009 mol) pyromellitic dianhydride, 5 mL (0.018 mol) 1,4-difluorobenzene, 25 mL dry nitromethane and 4.800g (0.036 mol) $AlCl_3$, the exact procedure used for compound **2** was followed. The intermediate ketoacids 2.100 g were obtained with 50% yield. After cyclization 0.905 g of the crude tetrafluoropentacenediquinone were obtained with 46% yield. After recrystallization

from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 0.700g of a yellow solid was obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1681 (C=O carbonyl), 1583 (C=C aromatic), 1470, 1452, 1415, 1391, 1320, 1255, 1212, 837, 732, 556. ^1H NMR (DMSO- d_6): δ 8.70 (s, 1H), 7.88 (dd, $J_1 = 8$ Hz, $J_2 = 2$ Hz, 1H). HRMS calcd. for $\text{C}_{22}\text{H}_6\text{F}_4\text{O}_4$: 410.0202, found 410.0180.

2,9-Difluoro-3,10-dinitro-; 2,10-difluoro-3,9-dinitropentacenediquinone (4a and 4b)

A mixture of 0.700g (0.002 mol) compound **2** (2,9-difluoro- and 2,10-difluoro pentacenequinone) were dissolved in 5 mL concentrated H_2SO_4 . To the resulting brown solution was added dropwise 7 mL of a 1:1 mixture of HNO_3 and H_2SO_4 . After the addition was finished, the flask was heated at 65 °C for 4 hours. The solution was then poured on ice and the yellowish precipitate filtered over a small frit. **4 a** and **4 b**: 0.721g (83 %), m.p. = 247 – 270 °C with decomposition, IR (KBr cm^{-1}): 1684 (C=O carbonyl), 1600 (C=C aromatic), 1555 and 1485 (NO_2 group), 1339, 1285, 944, 719. MS (m/e) = 464 (100).

2,9-; 2,10-Dinitropentacenediquinone (5a and 5b)

Pentacenediquinone, 1.000g (0.003 mol) was added into a round bottomed flask and dissolved in 5 mL concentrated H_2SO_4 . The flask was then placed on ice and to the solution was added dropwise 7 mL of a 1:1 mixture of HNO_3 and H_2SO_4 . Following this addition, the flask was heated at 65 °C for 4 hours. The solution was then poured on ice and the yellowish precipitate filtered over a small frit. After drying in the vacuum oven at 120 °C, 1.100g (89 %) of a beige precipitate was obtained. m.p. = 210 – 245 °C with decomposition. IR (KBr cm^{-1}): 1683 (C=O carbonyl), 1592 (C=C aromatic), 1538 and 1480 (NO_2 group), 1375, 1316, 1177, 1069, 1006, 887, 851, 710. HRMS calcd. for $\text{C}_{22}\text{H}_8\text{N}_2\text{O}_8$: 428.0280, found 428.0298.

2,9-; 2,10-Dichloropentacenediquinone (6a and 6b)

Starting with 4.000g (0.018 mol) pyromellitic dianhydride and 50 mL of chlorobenzene, the exact procedure used for compound **2** was followed. The intermediate ketoacids (6.000g) were obtained with 80% yield. After cyclization, resulted 2g (63%) of crude pentacenediquinones. After recrystallization from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 1.1000g of a yellow solid are obtained. m.p. > 400 °C; IR(KBr cm^{-1}

¹): 1683 (C=O carbonyl), 1587 (C=C aromatic), 1472, 1337, 1286, 1257, 1075, 994, 943, 922, 845, 713. HRMS calcd. for C₂₂H₈Cl₂O₄: 405.9799, found 405.9812.

Dichloroketoesters (6''a and 6''b)

The same synthetic procedure as in the case of fluoroketoesters **2''a** and **2''b** has been employed. Starting from 8.000 g pyromellitic anhydride, 22.000 g of ketoesters mixture was obtained with 70% yield.

Dichloroketoester (6''a)

6''a: 7.340 g (54%), m.p.= 232 °C; IR (KBr cm⁻¹): 1719 (C=O carbonyl ester), 1683 (C=O carbonyl), 1588 (C=C aromatic), 1485, 1401, 1302 – 1012 (C-O ester), 949, 921. ¹H NMR (DMSO-d₆): δ 8.06 (s, 1H), 7.8 (d, J = 12 Hz, 2H), 7.63 (d, J = 8 Hz, 2H), 4.07 (q, J = 8 Hz, 2H), 1.03 (t, J = 8 Hz, 3H). ¹³C NMR (DMSO-d₆): δ 193.6, 164.0, 141.7, 138.8, 134.8, 132.3, 131.1, 129.2, 129.0, 62.0, 13.4. HRMS calcd. for C₂₆H₂₀Cl₂O₆: 498.0751, found 498.0641.

Dichloroketoacid (6'a)

The same procedure as for the preparation of compound **2'a** was used. **6'a**: 4.600.g (70%), m.p.=321 °C; IR (KBr cm⁻¹): 3500 – 3000 (OH carboxylic acid), 1698 (C=O carboxylic acid), 1681 (C=O carbonyl), 1588 (C=C aromatic), 1498, 1401, 1365 – 1091 (C-O carboxylic acid), 947, 916, 843, 795. ¹H NMR (DMSO-d₆): δ 13.8 (s, 1H), 7.95 (s, 1H), 7.75 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H). ¹³C NMR (DMSO-d₆): δ 194.1, 165.7, 141.8, 138.5, 133.4, 131.0, 129.0. HRMS calcd. for C₂₂H₁₂Cl₂O₆: 442.0136, found 442.0036.

2,9-Dichloropentacenediquinone (6a)

Starting with the acid **6'a** (1.000g) and following the general procedure for the cyclization in AlCl₃ melt, 0.700g of **6a** have been obtained with 77% yield. The quinone was recrystallized from hot nitrobenzene producing 0.500g of golden prisms of **6a**. m.p. > 400 °C, IR (KBr cm⁻¹): 1683 (C=O carbonyl), 1587 (C=C aromatic), 1337, 1288, 1251, 995, 943, 847, 714. HRMS calcd. for C₂₂H₈Cl₂O₄: 405.9979, found 405.9812.

Dichloroketoester 6''b

6''b: 6.300 g (46%), m.p.= 120 °C; IR (KBr cm^{-1}): 1725 (C=O ester), 1683 (C=O carbonyl), 1588 (C=C aromatic), 1485, 1401, 1302 – 1012 (C-O ester), 949, 921. ^1H NMR (CDCl_3): δ 8.76 (s, 1H), 7.70 (d, J = 8 Hz, 2H), 7.45 (d, J = 8 Hz, 2H), 7.35 (s, 1H), 4.14 (q, J = 8 Hz, 2H), 1.09 (t, J = 8 Hz, 3H). ^{13}C NMR (CDCl_3): δ 194.0, 164.2, 144.8, 140.3, 134.6, 132.3, 130.9, 130.8, 130.7, 130.0, 1129.1, 126.6, 62.4, 13.7. HRMS calcd. for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{O}_6$: 498.0751, found 498.0641.

Dichloroketoacid 6'b

The same procedure used for the preparation of compound **2'a** was followed. **6'b:** 4.500 g (80%), m.p.= 264.4 °C; IR (KBr cm^{-1}): 3500 – 3000 (OH carboxylic acid), 1701 (C=O carboxylic acid), 1681 (C=O carbonyl), 1587 (C=C aromatic), 1498, 1401, 1363 – 1123 (C-O carboxylic acid), 1091, 947, 916, 843, 795. ^1H NMR (DMSO-d_6): δ 13.8 (s, 1H), 8.55 (s, 1H), 7.7 (d, J = 8 Hz, 2H), 7.6 (d, J = 8 Hz, 2H), 7.5 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 193.9, 165.4, 144.4, 138.3, 134.9, 131.4, 131.0, 128.8, 127.1, 126.5. HRMS calcd. for $\text{C}_{22}\text{H}_{12}\text{Cl}_2\text{O}_6$: 442.0136, found 442.0036.

2,10-Dichloropentacenediquinone (6b)

Starting with the acid **6'b** (2.000g) and following the general procedure for the cyclization in AlCl_3 melt, 1.500g of **6b** have been obtained with 83 % yield. The quinone was recrystallized from hot nitrobenzene producing 1.400g golden silvery flakes of **6b**. m.p. > 400 °C; IR (KBr cm^{-1}): 1686 (C=O carbonyl), 1587 (C=C aromatic), 1337, 1286, 1251, 995, 943, 847, 714. HRMS calcd. for $\text{C}_{22}\text{H}_8\text{Cl}_2\text{O}_4$: 405.9799, found 405.9812.

1,3,8,10-; 1,3,9,11-Tetrachloropentacenediquinone (7a and 7b)

Starting with 2.000g (0.009 mol) pyromellitic anhydride and 30 mL dry 1,3-dichlorobenzene, the exact procedure used for compound **2** was followed. The intermediate ketoacids (3.650 g) were obtained with 78% yield. After the cyclization, 0.339 g of the tetrachloropentacenediquinone was obtained with 10% yield. After recrystallization from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 0.187g of a yellow precipitate was obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1681 (C=O carbonyl), 1569 (C=C aromatic), 1421, 1265, 1225, 1007, 879, 804, 726, 712. HRMS calcd. for $\text{C}_{22}\text{H}_6\text{Cl}_4\text{O}_4$: 473.9020, found 473.8991.

2,3,9,10-Tetrachlororopentacenediquinone (8a,b and c)

Starting with 2.000g (0.009 mol) pyromellitic dianhydride and 30 mL 1,2-dichlorobenzene the exact procedure used for compound **2** was followed. The intermediate ketoacids (1.965 g) were obtained with 42% yield. After the cyclization, 0.420 g of the tetrachloropentacenediquinone was obtained with 23% yield. After recrystallization from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 0.390g of a yellow solid was obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1680 (C=O carbonyl), 1577 (C=C aromatic), 1453, 1262, 1119, 1030, 984, 910, 792. HRMS calcd. for $\text{C}_{22}\text{H}_6\text{Cl}_4\text{O}_4$: 473.9020, found 473.8991.

1,2,4,8,9,11-;1,2,4,8,10,11-Hexachloropentacenediquinone (9a and 9b)

Starting with 2.000g (0.009 moles) pyromellitic dianhydride and 30 mL dry 1,2,4-trichlorobenzene, the exact procedure used for compound **2** was followed. The intermediate ketoacids (5.217 g) were obtained with 60% yield. After the cyclization, 1.152 g of the hexachloropentacenediquinone was obtained with 23% yield. After recrystallization from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 0.350g of a yellow precipitate was obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1681 (C=O carbonyl),

1548 (C=C aromatic), 1423, 1351, 1281, 1205, 1025, 799. HRMS calcd. for $C_{22}H_4Cl_6O_4$: 541.8201, found 541.8243.

1,4,8,11-Tetramethylpentacenediquinone (10)

Starting with 2.000g (0.009 mol) pyromellitic dianhydride and 30 mL 1,4-dimethylbenzene the exact procedure used for compound **1** was followed. The intermediate ketoacids (3.617 g) were obtained with 93% yield. After the cyclization, 2.282 g of the tetramethylpentacenediquinone was obtained with 69% yield. After recrystallization from hot nitrobenzene and sublimation at 450 °C and 10^{-5} torr, 2.019g of a brown precipitate was obtained. m.p. > 400 °C; IR (KBr cm^{-1}): 1667 (C=O carbonyl), 1541 (C=C aromatic), 1380, 1320, 1233, 1175, 735. HRMS calcd. for $C_{26}H_{18}O_4$: 394.1205, found 394.1209.

2,9-; 2,10-Di(tert-butylphenyl)etherpentacenediquinone (11a and 11b)

In a very dry three neck round bottomed flask equipped with magnetic stirring, argon inlet, Dean-Stark trap and reflux condenser were added 0.3g (0.002mol) 4-tert-butylphenol, 0.828g (0.006 mol) K_2CO_3 , 25 mL toluene and 5 mL anhydrous DMF. The

mixture was heated at 120 °C for 2 hours until most of K_2CO_3 has been consumed and a yellowish color appeared. The temperature was raised to 150 °C and toluene distilled into the Dean-Stark trap. When all the toluene has been removed, 0.430g (0.001 mol) of quinone mixture **2** and another 5 mL of anhydrous DMF were added to the flask. Upon the addition of the quinone the solution turned a green color. The reaction was allowed to proceed overnight. The mixture was cooled to room temperature and poured on ice. The solid was filtered by suction and dried in a vacuum oven at 150 °C for 24 hours, giving 0.692g (90 %) of product. m.p. > 400 °C; IR (KBr cm^{-1}): 1677 (C=O carbonyl), 1589 (C=C aromatic), 1507, 1405, 1274 – 1170 (C-O ether). HRMS calcd. for $\text{C}_{42}\text{H}_{34}\text{O}_6$: 634.2355, found 634.2360.

2,9-Di(tert-butylphenyl)etherpentacenediquinone (**11a**)

The compound was synthesized using the same procedure as outlined above but starting from the pure 2,9-difluoropentacenediquinone **2a**. m.p. > 400 °C; IR (KBr cm^{-1}): 1677 (C=O carbonyl), 1589 (C=C aromatic), 1507, 1405, 1274 – 1170 (C-O ether). ^1H NMR (CDCl_3): δ 9.09 (s, 1H), 8.27 (dd, $J_1 = 8.8$ Hz, $J_2 = 2$ Hz, 1H), 7.73 (s, 1H), 7.39 (d, $J = 10$ Hz, 2H), 7.33 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1H), 6.98 (d, $J = 10$ Hz, 2H), 1.3 (s, 9H). ^{13}C NMR (CDCl_3): δ 180.5, 179.5, 163.0, 151.0, 147.5, 136.9, 135.8, 134.5, 139.5, 126.9, 126.2, 125.1, 123.3, 120.0, 114.3, 34.7, 31.4. HRMS calcd. for $\text{C}_{42}\text{H}_{34}\text{O}_6$: 634.2355, found 634.2360.

2,10-Di(tert-butylphenyl)etherpentacenediquinone (11b)

The compound was synthesized using the same procedure as outline above but starting from the pure 2,10-difluoropentacenediquinone **2b**. m.p. > 400 °C; IR (KBr cm⁻¹): 1678 (C=O carbonyl), 1590 (C=C aromatic), 1505, 1410, 1364 – 1019 (C-O ether), 799. ¹H NMR (CDCl₃): δ 9.09 (s, 1H), 8.26 (dd, J₁ = 8.8 Hz, J₂ = 2 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 1.3 (s, 9H). ¹³C NMR (CDCl₃): δ 181.5, 180.5, 164.0, 152.0, 148.5, 136.9, 136.8, 135.5, 130.5, 127.9, 127.2, 127.1, 123.3, 120.0, 114.3, 34.7, 31.4. HRMS calcd. for C₄₂H₃₄O₆: 634.2355, found 634.2360.

1,4,8,11-Tetra(tert-butylphenyl)etherpentacenediquinone (12)

The compound was synthesized using the same procedure as outlined above but starting from 1,4,8,11-tetrafluoropentacenediquinone **3**. m.p. > 400 °C; IR (KBr cm⁻¹): 1677 (C=O carbonyl), 1590 (C=C aromatic), 1507, 1487, 1364, 1322 – 1002 (C-O ether), 946, 921, 849, 724. ¹H NMR (CDCl₃): δ 9.1 (s, 1H), 8.25 (dd, J₁ = 8 Hz, J₂ = 1.6 Hz, 1H),

7.36 (d, J = 11.6 Hz, 2H), 7.32 (dd, J₁ = 8 Hz, J₂ = 2.8 Hz, 1H), 6.95 (d, J = 11.6 Hz, 2H), 1.3 (s, 9H). ¹³C NMR (CDCl₃): δ 180.5, 164.0, 151.9, 148.5, 135.5, 130.5, 127.2, 123.3, 120.0, 114.3, 34.5, 31.4.

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Chapter III. Electroactive Pentacenediquinones

The redox behaviour of quinones has attracted a strong interest for many years and a very large number of papers have been published regarding this subject. Quinones are long known for their ability to accept electrons and reversibly change colours upon electrochemical reduction and oxidation. Simple quinone/hydroquinone couples are probably the most investigated organic redox couples.

III.1. Electrochemistry of Quinones

Quinone/hydroquinone couples are readily available for electrochemical studies. Cyclic voltammetry is a common method to study the electrochemistry of quinones. Often the first step in the electrochemical characterization of a compound is to ascertain its oxidation-reduction reversibility. Therefore, cyclic voltammetry is considered to be the most convenient technique for this purpose.

III.1.1. Cyclic Voltammetry

In cyclic voltammetry the potential of a small stationary working electrode is changed linearly with time, starting from a potential where no electrode reactions occurs and moving to potentials where reduction or oxidation of the compound being studied occurs.^{1,2,3} After traversing the potential region in which one or more electrode reaction take place, the direction of the linear sweep is reversed and the electrode reaction of intermediates and products formed during the forward scan can often be detected. The current response is plotted as a function of the applied potential.^{1,3}

The time scale of the experiment controlled by the scan rate and the total potential traversed can be varied over the range of 10^2 to 10^{-5} s. In most cases there is very little difference between the first cycle and successive scans.^{1,2,3}

A supporting electrolyte is also present to enhance conductivity and repress migration of charged reactants and products. The supporting electrolyte is chosen on the basis of solubility in a given solvent, as well as its inertness toward the electroactive substance and its electrolysis products. In nonaqueous solutions, tetraalkylammonium salts are the most commonly used electrolytes.¹

The choice of solvent in cyclic voltammetry is determined by several factors like the solubility of electrolyte and electroactive substance, and reactivity with electrolytic products. The solvent must also have other important properties such as decreasing unwanted effects like the adsorption of the electroactive species at the electrode.^{1,4}

The most commonly employed working electrodes in cyclic voltammetry are solid disk electrodes. Platinum, glassy carbon, gold, silver and amalgams are often used especially in nonaqueous electrochemistry and electrochemistry at positive potentials.¹ The most common reference electrodes used in aqueous solution are Ag/AgCl and the calomel electrode. If aqueous-based references are used in nonaqueous solution, often aqueous contamination of the nonaqueous cell can occur. Therefore, for nonaqueous electrochemistry, the use of an Ag/Ag⁺ reference is recommended.¹

Cyclic voltammetry is a direct method to measure the formal potential of a half reaction when both oxidized and reduced forms are stable during the time required to obtain the voltammogram or the current-potential curve.^{1,3} The cathodic peak in the cyclic voltammogram results from the competition of two factors, the increase in the net rate of reduction as the potential is made more negative, and the development of a thickening depletion layer across which the reactant must diffuse.¹ An anodic peak in the cyclic voltammogram is obtained when the surface concentration of anions becomes

small and the current is limited by the rate of return of the anions to the electrode.³ The cyclic voltammogram is characterized by several important parameters: the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials, the cathodic (i_{pc}) and anodic (i_{pa}) currents, and the half-wave potential ($E_{1/2}$).^{1,3}

$$E_{1/2} = E^{0'} + (RT/nF)\ln(D_R/D_0)^{1/2} \quad (1)$$

In equation (1) $E^{0'}$ is the formal potential pertaining to the ionic strength of the solution, D_0 and D_R are the diffusion coefficients of the oxidized and reduced form, and n is the number of electrons in the half reaction. Because $D_0 \sim D_R$, $E_{1/2}$ is usually within a few millivolts of $E^{0'}$ (2).

$$E_{1/2} = E^{0'} \pm 0.001 \quad (2)$$

The criteria of reversibility can be illustrated as (3):

$$\Delta E_p = E_{pa} - E_{pc} = 57/n \quad (3)$$

This value must be independent of the scan rate and concentration.^{1,3} Irreversibility manifests itself through (4):

$$\Delta E_p > 57/n \quad (4)$$

ΔE_p increases with increasing sweep rate.^{1,3}

The value of n as defined in the various cyclic voltammetry criteria for reversibility is usually equal to 1, occasionally 2.¹

III.1.2 Electrochemistry of Diquinones in Nonaqueous Solvents

In aprotic nonaqueous solvents monoquinones are reduced in two successive one-electron steps which are electrochemically reversible:

Figure III.1. Reduction of 1,4-benzoquinone

In the first wave the quinone accepts one electron producing a radical anion or semiquinone. In the next wave another electron is added producing a dianion (Figure III.1).⁵

In the case of substituted pentacenediquinones, more complex voltammograms are obtained. Due to the two quinone moieties present, conjugated diquinones provide voltammograms with four redox waves which interconvert the five stable oxidation states⁶: Q^0 (neutral), $Q^{\cdot-}$ (semiquinone or radical anion), Q^{2-} (dianion), Q^{3-} , Q^{4-} . For example, in the case of pentacenediquinone **1** the reduction waves can be observed in Figure III.2.

Figure III.2. Cyclic voltammogram of pentacenediquinone 1

For all the substituted pentacenediquinones, the voltammogram always indicates two reversible couples with roughly 60 mV peak separation and nearly equal anodic and cathodic currents, and a more complex process at more negative potentials. The anodic peak current of this third process is usually less than its cathodic peak, and the cathodic-anodic peak potentials are frequently separated by more than 100 mV, rather than the 60 to 30 mV separation expected for a one or a two reversible reduction. Relative to the first two reversible couples, this quasi-reversible couple has larger cathodic peak currents and it is most likely a two electron wave.⁶ For pentacenediquinone 1 Figure III.2 shows that this third wave is resolved into two very closely spaced couples.

In Table III.1 are presented the half-wave potentials for the series of prepared pentacenediquinones using DMF as the solvent and tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

Table III.1. Half-wave potentials vs. NHE for the semiquinone and dianion of substituted pentacenediquinone

Compound	E _{1/2} (mV)	
	Semiquinone Q ⁻	Dianion Q ²⁻
1	239	700
2a and 2b	200	642
3	220	656
6a and 6b	260	674
7a and 7b	179	577
8a, 8b and 8c	324	637
9a and 9b	179	537
10	342	750
11a and 11b	254	696
12	426	729

The substituent present on the aromatic ring can have a strong influence on the reduction potential. It can be observed from Table III.1. that pentacenediquinones containing the electron-withdrawing substituents are reduced more easily than pentacenediquinones containing the electron-donating groups. Electron-withdrawing groups facilitate reduction by lowering the LUMO energy, while the electron-donating substituents have an opposite effect.³

In general the behaviour of quinones in aprotic solvents can be altered by any perturbation on the diffusion layer concentrations of the quinone, semiquinone and dianion. Acid-base, ion-pairing and complex formation equilibria are the principal perturbation on those concentrations. These effects can simply shift the first or second reduction wave, or can completely eliminate waves.^{5,7}

The effect of ion-pairing and complex formation on the current potential curve of quinones has been studied in detail by Davies and Peover.⁵ Their study revealed that the radical anion forms a 1:1 complex with Li⁺ but not with Na⁺, K⁺, NEt₄⁺, NBu₄⁺. The order of complexing strength is Li⁺ > Na⁺ > K⁺ > NEt₄⁺ > NBu₄⁺. Also, the dianion is complexed by all these cations which shift the second reduction wave to more positive

potentials. Ion-pair formation is more prevalent in acetonitrile solution than in *N,N'*-dimethylformamide (DMF) and dimethylsulphoxide (DMSO), but tetraalkylammonium salts have been found to be completely dissociated in acetonitrile.⁵

III.2. Properties of Radical Anions of Pentacenediquinones

Near-infrared activity is the most important property for the radical anions of pentacenediquinones.

III.2.1. Near-Infrared (NIR) Absorbptions of Reduced Pentacenediquinones

Probably the most interesting property of conjugated diquinones reported in the literature is the NIR activity of anion radicals. These species absorb at a much longer wavelength than the anion radicals of monoquinones. Due to the lack of information about the NIR activity, Miller and his group prepared a series of substituted anthradiquinones and investigated their behaviour using spectroelectrochemical methods.^{6,11-14} The spectroelectrochemistry was performed in DMF using Bu₄NBF₄ as the supporting electrolyte. The results obtained by the Miller group are listed in Table III.2.

Table III.2. Spectroscopic and electrochemical data for anthradiquinones⁶

Compound	$\lambda_{\max}$ (nm) (log ϵ) ^b		E° (V, SCE)	
	Anion	Dianion
1335 (4.50)	880 (4.54)	-0.42	-0.92
1400 (4.19)	-	-0.41	-0.93
1480 (4.50)	886 (4.46)	-0.41	-0.89

1500 (4.11)	876 (4.27)	-0.31	-0.83
1200-1650 (4.00)	-	-0.30	-0.85
1560 (4.21)	866 (4.16)	-0.25	-0.74
1615 (4.16)	900 (4.26)	-0.05	-0.55
1200-1700 (4.00)	890 (4.14)	-0.08	-0.57
900 (3.65)	640 (3.74)	+0.14	-0.59
450	-	-0.43	-1.34
480 (3.71)	-	-0.61	-1.41
510 (3.76)	-	-0.69	-1.41

The monoquinone radical anions show strong bands in the 400 – 600 nm region. Comparison of the spectra shows that more rings in the quinone structure give modest shifts to longer wavelength. The electronic spectra of anthracenediquinone anions and derivatives are quite different. Instead of a band in the 400 – 600 nm region, the semiquinones of anthracenediquinones exhibit absorbance in the NIR region between

1300 and 1600 nm.^{6,10-13} Also, there seems to be a correlation between the type of substituent and absorbance peak. Electron-withdrawing substituents like Br and Cl move the band further into the NIR domain.

Neutral monoquinones display the absorbance around 330 nm. These bands have been assigned by Miller as π - π^* transitions and not n- π on the basis of their intensity. Nonreduced pentacenediquinone **1** also has a maximum absorbance at 335 nm. Hence, the longest π - π^* transition for diquinones is in the same region as for monoquinones. Therefore it is safe to assume that unreduced pentacenediquinone behaves like monoquinones.^{6,10,11}

Based on Miller's work and using unsubstituted pentacenediquinone as a benchmark, a series of substituted pentacenediquinones were investigated using spectroelectrochemical methods. The spectroelectrochemistry was also performed in DMF using the large and non-coordinating Bu_4N^+ as the counterion.

Similar to Miller's anthracenediquinones, instead of a peak between 400 and 600 nm, the semiquinones of pentacenediquinones present sharp peaks of absorbance between 1300 and 1550 nm.^{6,10-13} These bands appear at much longer wavelength than either 1,4-anthraquinone anion radical (510 nm) or anthracene anion radical (710 nm). In the case of radical anions of pentacenediquinones, the long wavelength bands have been postulated to arise from π^* - π^* transitions, SOMO – LUMO from a delocalized ground state. The SOMO – LUMO represents the difference in energy between two lowest unoccupied molecular orbital. SOMO has been defined as the lowest unoccupied orbital of the neutral molecule, and LUMO represents the lowest unoccupied molecular orbital for the radical anion.^{14,15} According to Miller these intense, low energy, sharp bands suggest

delocalization of the charge between two quinone moieties. In the case of charge transfer complexes, the shape of the absorbance peak would be broad rather than sharp.^{6,10}

It was also observed that the position of the substituent on the outside aromatic ring has an influence on the peak position in the NIR region (Table III.4). The presence of electron-withdrawing substituents has an influence on the band-gap. Electron-withdrawing substituents push the absorbance further into the NIR region by reducing the energy of the HOMO-LUMO band-gap and facilitating the transition of the odd electron. The semiquinone of tetrafluoropentacenediquinone **3** has the smallest band-gap (0.823 eV) and presents absorbance at the highest wavelength, 1508 nm.

The value of the band-gap for semiquinone and dianion was calculated using the corresponding $\lambda_{\max}$ value from the NIR spectra. The following equations can be used for the calculation of the band-gap:

$$E = hc/\lambda \quad (\text{J}) \quad (5)$$

where E (J) is energy, $h = 6.62 \times 10^{-34}$ (Js) represents Planck's constant, $c = 3 \times 10^8$ (m/s) represents the speed of light in vacuum, λ represents the maximum wavelength corresponding to the semiquinone and dianion peak. The band-gap can be then calculated:

$$E_g = E/1.6 \times 10^{-19} \quad (6)$$

where E_g is the band-gap (eV) and 1.6×10^{-19} (C) represents the elementary charge.

Table III.3. NIR peaks for the semiquinone and dianion

No. Compound	Structure	Semiquinone		Dianion	
		$\lambda_{\max}$ (nm)	Calculated band-gap (eV)	$\lambda_{\max}$ (nm)	Calculated band-gap (eV)
1		1335	0.925	880	1.412
2	and isomer	1360	0.921	890	1.40
3		1508	0.823	1007	1.233
4	and isomer	1430	0.868	930	1.334
5	and isomer	1400	0.886	890	1.394
6	and isomer	1372	0.905	890	1.394
7	and isomer	1456	0.852	934	1.329
8	and isomers	1430	0.868	890	1.394
9	and isomer	1400 - 1600	Not available	Not observed	Not available
10		1370	0.920	890	1.394
11	R = O-Ph-tBu and isomer	1331	0.933	880	1.412

12	R = O-Ph-tBu	1330	0.933	880	1.412
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The experimental data presented in Table III.3. confirms the fact that electro-withdrawing substituents like F, Cl, NO₂ move the absorbance further into the NIR region closer to 1550 nm. The spectroelectrochemistry is fully reversible and does not leave any residual NIR absorbance.

The number of substituents and their position on the external aromatic rings is also of importance. For example, the semiquinone of tetrafluoropentacenediquinone **3**, has four fluorine atoms in the immediate vicinity of the carbonyl, and exhibits a maximum absorbance at 1509 nm. In the case of the other two fluorinated pentacenediquinones (2,9 and 2,10 difluoro), the semiquinone absorbs only at 1360 nm. The semiquinone of compound **7** that has four chlorine atoms on the external aromatic rings, with only two in proximity of the carbonyl, shows absorbance at 1456 nm. The semiquinone of hexachloropentacenediquinone **9** exhibits a broad and featureless absorbance between 1200 and 1600 nm. In this case the formation of the dianion was not observed.

In the case of pure isomers, the position of the NIR maximum for the semiquinone changes only by 2 to 5 nm when compared to the isomeric mixture. For the dietherpentacenediquinone **11** the NIR maximum appears at 1331 nm in the case of 2,10 isomer, and also in the case of the mixture, when both isomers are present (Figure III.3). Therefore, solely for the purpose of NIR investigations, the separation of the isomers is unnecessary.

Figure III.3. UV-Vis-NIR spectra of: (a) compound **11** as a mixture, and (b) compound **11b** as the pure isomer

By comparing the NIR absorptions between Miller's anthraquinones similar in structure with some of the substituted pentacenediquinones it can be observed that for both type of compounds the substitution pattern plays an important role (Table III.4).

Table III.4. Comparison between the NIR absorption of anthraquinones and pentacenediquinones

Substituted anthraquinones			Substituted pentacenediquinones		
Compound	NIR absorption [nm]		Compound	NIR absorption [nm]	
	Semiquinone	Dianion		Semiquinone	Dianion
1335	880	1	1335	880
1480	886	10	1370	890
1615	900	3	1508	1007

For example the semiquinone of tetramethylantranthraquinone displays absorption at 1480 nm. In a similar way the semiquinone of compound **10** displays absorption at 1370 nm compared to 1335 nm for the semiquinone of compound **1**. Also the type of substituent, electron-donating versus electro-withdrawing is also of importance. The semiquinone of tribromoanthraquinone absorbs at 1615 nm compared to 1480 nm for the semiquinone of tetramethylantranthraquinone. In the case of pentacenediquinones, the semiquinone of compound **3** displays absorption at 1508 nm compared to 1370 nm for the semiquinone of compound **10**.

Based on the experimental observations for Miller's anthraquinones and our series of pentacenediquinones, it can be concluded that a compound must fulfill some structural requirements in order to display NIR absorption (Table III.2 and Table III.3). First, two quinone moieties must be present in the molecule, and also the carbonyl groups must be separated by an aromatic ring. In the case of substituted pentacenediquinones, in order to shift the NIR activity further into the IR domain, at least four electron-withdrawing substituents positioned in the proximity of carbonyl are necessary.

III.2.1.1 Electrolyte Dependency Study

To check the solvent and electrolyte dependence, spectroelectrochemical studies of the NIR activity of the pentacenediquinones series were done in strong solvating agents like DMSO and DMF. Unfortunately, no other solvents were used for this study due to the insolubility of the pentacenediquinones. As supporting electrolytes were used LiClO_4 to supply the small and strong coordinating counterion Li^+ , Bu_4NClO_4 and Bu_4NPF_6 to supply the large and noncoordinative counterion Bu_4N^+ .

A variation of the counterion from Bu_4N^+ to Li^+ resulted in no change whatsoever in the observed spectra (peak position) measured in DMF or in DMSO. This result indicates that the anions are freely solvated in these solvents and the nature of the counterion is of no consequence (Table III.5.). When the study is performed using Bu_4N^+ as a counterion, the spectroelectrochemistry is fully reversible and does not leave any residual NIR absorbance. However when the counterion is Li^+ , upon reoxidation some residual NIR absorbance is observed and in some cases the radical dianion does not form. This is probably due to the formation of a very stable insoluble complex between the semiquinone and the small, strongly coordinating cation Li^+ . The results of this study are presented in Table III.5. The position of the absorbance peak in the NIR region varies very little (1 to 5 nm) with the solvent and electrolyte used for both semiquinone and dianion. This investigation confirms that the NIR absorbance of reduced pentacenediquinones is not dependent upon solvent and electrolyte.

Table III.5. Electrolyte dependency study

Electrolyte and solvent	Reduced species	Compound and peak position after reduction (nm)			
		1	2 (mixture of isomers)	5 (mixture of isomers)	11 (mixture of isomers)
LiClO ₄ /DMSO	Q ⁻	1327	1340	1415	1333
	Q ²⁻	Not observed	874	890	Not observed
Bu ₄ NClO ₄ /DMSO	Q ⁻	1326	1344	1410	1335
	Q ²⁻	887	870	900	875
LiClO ₄ /DMF	Q ⁻	1328	1350	Not observed	1333
	Q ²⁻	Not observed	Not observed	Not observed	Not observed
Bu ₄ NClO ₄ /DMF	Q ⁻	1331	1349	1418	1335
	Q ²⁻	885	885	870	875
Bu ₄ NPF ₆ /DMF	Q ⁻	1332	1350	1424	1331
	Q ²⁻	880	888	928	880

III.3. Potential Applications

Novel NIR electrochromic materials enable the design of devices using low insertion loss configuration. Insertion loss in an optical fiber is due to the methods of coupling the fiber to the power, as well as absorption, dispersion, scattering and diffusion. Compounds that absorb in the NIR region could one day find applications in the field of optical fibres as electrochromic variable optical attenuators. It is known that fiber optics operate in three windows; the first one between 800 and 900 nm, the second one between 1200 and 1350 nm, and finally the last generation of fibre optic between 1500 and 1600 nm (Figure III.4).

Figure III.4. Attenuation windows

A variable optical attenuator operates in one of the telecom windows in a simple way. The light is focused via an input collimator, passes through an electrochromic element and exits through an output collimator (Figure III.5.a). The electrochromic element consists of two electrodes, an anodic electrochromic layer, a cathodic electrochromic layer, and a gel electrolyte. Variable optical attenuation control is achieved by adjusting the applied voltage within the electrochromic element (Figure III.5.b).

Figure III.5. Conceptual drawing of fiber-based (a) Variable optical attenuator, (b) Electrochromic element

An electrochromic material to be used in a variable optical attenuator should fulfill some basic requirements; such as high NIR absorbing in one stable state, no or very little NIR absorbing in another stable state, good switching speed (ms). In terms of optical properties such a material must have low optical loss (e.g., <0.5 dB/cm). Also, the material should be stable to water, heat, electrical breakdown and light. Finally, these compounds must be processable in terms of film forming ability and patterning ability on the electrode.

Substituted pentacenediquinones satisfy some of these requirements such as NIR absorbance in one stable state and switching cycles, as they do not degrade, decompose or lose intensity in the NIR region. The radical anions and dianions of the synthesised pentacenediquinones **1**, **3** and **11** are found to basically cover all three telecom windows (Figure III.6).

Figure III.6. Typical NIR absorptions of the radical anions and dianions of pentacenediquinones **1**, **3** and **11**

However, the major problems that small molecules have are film formation, patterning ability and adhesion on the electrode surface. Therefore, the next chapter will focus on the synthesis, characterization and properties investigation of polymers prepared from substituted pentacenediquinones.

III.4. Conclusion

The electrochemistry and NIR properties of the series of pentacenediquinones were investigated using spectroelectrochemical methods. The semiquinones and radical dianions for pentacenediquinones display absorption in all three telecom windows. However, in order to display NIR absorption the compounds must fulfill some structural

requirements. Two quinone moieties separated by at least one aromatic ring are necessary for these compounds in order to display such low energy transitions. The type of substituent and its position on the external aromatic rings are also of importance. Electron-withdrawing substituents closer to the carbonyl move the absorption further down into the NIR domain. In conclusion, in this chapter was established and demonstrated the correlation between structure and the NIR absorption of the reduced pentacenediquinones.

III.5. Experimental

Materials

Tetrabutylammonium hexafluorophosphate, tetrabutylammonium perchlorate, lithium perchlorate, electrochemical grade *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) have been purchased from Aldrich and used as received.

Cyclic Voltammetry

Cyclic voltammetry was performed using a BAS 3C stand (Figure III.7); samples were degassed with argon and stirred continuously between measurements. Two sets of measurements were taken, one in DMF and another one in DMSO.

Figure III.7. Cyclic voltammetry setup

A glassy carbon electrode was used as the working electrode, silver wire was used as the reference electrode and platinum wire was used as the counter electrode. Scan rates between 50 and 1000 mV/s were employed in all studies.

Spectroelectrochemistry

The spectroelectrochemical generation of the semiquinone and diradical anion was performed in an optical transparent cell (OTTLE cell).¹⁷ An OTTLE cell is composed of: a steel plate (a), an inlet (b), Teflon gasket (c), front and back KBr windows (d,f), a polyethylene spacer containing melt-sealed electrodes, a Teflon holder and the back plate (Figure III.8.A). The polyethylene spacer contains a system of three electrodes: a gold minigrid working electrode (a), a platinum counter electrode (b) and a silver wire pseudoreference electrode (c) (Figure III.8.B).

Figure III.8. Scheme of an OTTLE cell¹⁷

The samples were dissolved in the electrolyte solution, filtered, and the clear solution injected in the OTTLE cell. Various negative potentials from -250 to -1400 mV were applied to the cell and the response spectra recorded using a Lambda 900 UV-Vis spectrophotometer.

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Chapter IV. Electroactive Pentacenediquinone-Containing Polymers

Polymers containing a redox active moiety like quinones are the subject of recent interest due to their redox behaviour as well as their conductive and optical properties. Halogenated pentacenediquinones can be used as monomers to prepare a series of pentacenediquinone-containing polymers. These polymers are expected to display very interesting electrical and spectroelectrochemical properties arising from the pentacenediquinone moiety, either in solution or in the solid state (e.g. film).

IV.1. Electroactive Polyanthraquinones

In spite of the strong interest in both quinones and conjugated polymers, polyanthraquinones having π – conjugation along the main chain have received much less attention, presumably due to the difficulty in preparing such polymers. The reported preparative methods for the synthesis of conjugated anthraquinone containing polymers include organometallic dehalogenation using a zero - valent nickel complex (NiL_m) and dehalogenation with metallic copper has contributed to the preparation of some polyquinones (Scheme IV.1).¹⁻³ Organometallic dehalogenation allows the preparation of not only polyanthraquinones but also of some mixed poly(anthraquinone thiophene)s.³ Such polymers contain a repeating unit that has a fused ring with a thiophene unit at both ends and a long alkyl chain to control self-assembly.

Scheme IV.1. Known poly(anthraquinone)s prepared via Ni and Cu polycondensation^{2,3}

Polyanthraquinones are electrochromic and undergo a visible colour change depending on the applied potential. For example, the polymer containing thiophene moieties (Scheme IV.1) presents a remarkable colour change from yellow to purple (Figure IV.2).^{2,3}

Figure IV.1. Cyclic voltammogram of the poly(anthraquinone thiophene)²

Polyanthraquinones (Scheme IV.1) also show an increase in conductivity of a few orders of magnitude from 10^{-8} to 10^{-5} S/cm after doping with sodium naphthalenide, which places these compounds in the range of semiconductors.¹

Electrochromism and electrical conductivity of quinones, as well as the ability to influence self-assembly, solubility and film formation by slight modification of the structure has raised the question if it is possible to obtain such interesting polymers using pentacenediquinones as monomers.

From the series of substituted pentacenediquinones presented in Chapter II, the dihalogenated (F, Cl) pentacenediquinones can be used as potential monomers for polymerization. However, in this case the nickel or copper coupling cannot be the synthetic method of choice. Due to the poor solubility of pentacenediquinone monomers, this method would only produce oligomers. A relatively high molecular weight of polymer is a prerequisite for forming a good film. Therefore, it was necessary to introduce a flexible moiety inside the repetitive unit. This can be achieved using, for example, large bulky bisphenols that will introduce solubility into the polymer chains.

The results of previous research points towards the preparation of poly(aryl ether)s, namely poly(aryl ether quinone)s rather than polyanthraquinones.

IV.2. Poly(aryl ether)s

Poly(aryl ether)s are a family of “engineering thermoplastics”. They are made on a smaller scale and at higher cost than commodity plastics, but have remarkable mechanical and thermal properties.⁴ Poly(aryl ether)s possess, like other aromatic polymers, a high degree of thermal stability but also good processability. Their ability to

be processed is linked to the presence of the ether bond. Without it, the polymers would only have good thermal stability but would be too infusible and insoluble to be processed.⁵ Poly(aryl ether)s can be prepared mainly by four synthetic methods: aromatic electrophilic substitution, metal-catalyzed aryl-aryl coupling, ring-opening polymerization and aromatic nucleophilic substitution. The last one is the most common synthetic method used for the preparation of poly(aryl ether)s.⁴

IV.2.1. Polymerization via Nucleophilic Aromatic Substitution

Polymerization via nucleophilic aromatic substitution requires the use of a bisphenol and an activated dihalide monomer. The dihalide must contain an electron – withdrawing group, usually in the *para* position to the halide (Scheme IV.2).

Scheme IV.2. General reaction scheme for nucleophilic aromatic substitution

The reaction takes place in a polar, aprotic solvent such as *N*-methyl pyrrolidinone (NMP), dimethylsulphoxyde (DMSO) or *N,N*-dimethylacetamide (DMAc) and requires the presence of an alkali base. The polymerization of bisphenoxides with activated dihalides is believed to proceed through a S_NAr mechanism. The first step involves the attack on the aryl halide by the nucleophile to form a Meisenheimer complex that is stabilized by the presence of the electron - withdrawing group (Figure IV.3). The formation of the complex is quickly followed by the loss of the leaving group.⁶

Figure IV.2. Resonance structures of the Meisenheimer complex

There are several factors that influence the success of aromatic nucleophilic substitution.⁷ The stoichiometry of the reagents is crucial for attaining high molecular weight. Another important factor would be the ability of the electron-withdrawing group to stabilize the Meisenheimer complex. The electron-withdrawing groups usually vary from simple ketones and sulfones to triazoles or benzimidazoles.⁸

The rates of S_NAr reactions are greater for activated aryl difluorides than the chloride analogues.⁶ This result is due to the fluorine's large electronegativity which increases the net charge density on the carbon to which it is attached. The displacement of fluorine from activated monomers is favoured over other halides.⁶ Therefore, aryl difluorides are usually preferred over other dihalides for this type of polycondensation.

IV.3. Synthesis of Poly(aryl ether quinone)s

Using nucleophilic displacement of aryl halides as the synthetic method of choice, a variety of poly(aryl ether quinone)s can be prepared starting from dihalogenated pentacenediquinones. As well, the option was made for difluoropentacenediquinones over their dichloro counterparts due to the increased reactivity of aryl difluorides.

Difluorinated pentacenediquinones were reacted with various bisphenols to produce a series of four polymers that are expected to be more soluble than their pentacenediquinone counterparts (Scheme IV.3). The bisphenols chosen for this polymerization are 4,4'-(isopropylidene)diphenol or bisphenol A (BPA), 4,4'-

(hexafluoroisopropylidene)diphenol or hexafluoro bisphenol A (6F-BPA) and 9,9-bis(4-hydroxyphenyl)fluorene or fluorene bisphenol (FB) in order to impart solubility to the polymers.

Scheme IV.3. Synthetic route to poly(aryl ether quinone)s

Potassium carbonate was used as a base, and the reaction solvent was sulfolene (tetramethylene sulfone). The reaction requires usually eight hours of reflux and the yields vary between 80 – 100%.

IV.4. Characterization of Poly(aryl ether quinone)s

The polymers were characterized mainly by infrared (IR) spectroscopy, differential scanning calorimetry (DSC) and inherent viscosity (η_{inh}). Due to the poor

solubility of poly(ether quinone)s in common NMR solvents, the NMR spectra could not be obtained.

IV.4.1. Infrared Spectroscopy

The IR spectrum of each polymer displayed C=O stretching band in the range from 1670 to 1688 cm^{-1} . The C=C stretching band derived from the aromatic bond from 1485 to 1587 cm^{-1} can also be observed, as well the stretching from the C-O bond between 1100 and 1300 cm^{-1} (Figure IV.3).

Figure IV.3. IR of poly(aryl ether quinone) 13

IV.4.2. Glass Transition Temperature

The glass transition temperatures (T_g) were determined by differential scanning calorimetry. All poly(aryl ether quinone)s displayed high T_g 's due to the presence of aromatic rings and some rigidity within the polymer chain. In Table IV.1 are presented the glass transition temperatures of the prepared polymers.

Table IV.1. Glass transition temperatures and inherent viscosities of the poly(aryl ether quinone)s

Polymer	T _g (°C)	η _{inh} (dL/g) at 25 °C
13	80	0.05
14	271	0.3
15	180	0.2
16	Not observed	0.7

IV.4.3. Inherent Viscosity

Solution viscosities were measured at concentration of 0.5g/100 mL of solvent by determining the flow time of a certain volume of solution through a capillary of fixed length. Flow time in seconds is recorded as the time for the meniscus to pass between two designated marks on the viscometer⁹. The measurements are always run at a constant temperature.

The inherent viscosity, η_{inh}, is defined as

$$\eta_{inh} = (\ln t/t_0)/C \quad (\text{dL/g}) \quad (7)$$

where C is the solution concentration in grams per 100 mL solvent, and time t and t₀ are in seconds.⁹

In Table IV.1 are presented the inherent viscosities for the polymer series. The measurements were done at 25 °C in NMP. Usually, for poly(aryl ether)s viscosities under 0.1 dL/g indicate oligomers, values between 0.1 and 0.3 dL/g indicate low molecular weight polymers, and values above 0.5 dL/g indicate high molecular weight polymers. It can be observed from Table IV.1 that with exception of polymer **16**, polymers **13** to **15** are low molecular weight polymers.

IV.5. Cyclic Voltammetry

The electrochemical properties of the poly(aryl ether pentacenediquinone)s arise from the diquinone moiety. Therefore, the spectroelectrochemical behaviour of these polymers is expected to be very similar if not identical with the behaviour of pentacenediquinones. Cyclic voltammetry (CV) was used to investigate the electrochemistry of these polymers, with the exception of the polymer **16** containing NO₂ groups. Due to the fact that the NO₂ group is also susceptible to reduction, polymer **16** was investigated only by the spectroelectrochemical method in an optical transparent thin layer (OTTLE) cell. The CV data were obtained in anhydrous DMF and 0.1M Bu₄NPF₆ as the supporting electrolyte and a polished glassy carbon electrode. Ferrocene, with an E_{1/2} of 634 mV in DMF, was used as an internal standard and a platinum wire was used as the counter electrode. The half-wave potentials (Table IV.2) are reported versus NHE.

Conjugated diquinones such as pentacenediquinone (**1**) show four reversible redox waves corresponding to five stable oxidation states. For compound **1** the voltammogram (Figure III.2) clearly indicates two reversible couples with 60 mV peak separation. From CV of the pentacenediquinone-containing polymers, two reduction waves corresponding to the radical anion (Q^{•-}) and the dianion (Q²⁻) can be readily observed (Figure IV.4). The cathodic and anodic peaks are frequently separated by more than 100 mV, rather than 60 mV that is characteristic for the one- or two- electron reversible reductions. The irreversibility of reduction observed in the case of pentacenediquinone-containing polymers may be due to the fact that both reduced species are more stable to oxidation than pentacenediquinones.

Figure IV.4. Cyclic voltammogram of polymer **13**

IV.6. Spectroelectrochemical Study

The absorption spectra of radical anion and dianion of these polymers **13-16** were obtained using an OTTLE cell containing a solution of 0.1M Bu₄NPF₆ in anhydrous DMF as electrolyte and were recorded on a UV-Vis-NIR spectrophotometer. Negative potentials between -250 and -1600 mV were applied to the cell.

Similar to the NIR activity of pentacenequinones (Chapter III.2.2), the radical anion of polymers **13-16** shows absorbance between 1335 nm and 1360 nm, and the diradical anion shows a peak between 880 and 940 nm (Figure IV.5). When a potential of -1200 mV is applied to the OTTLE cell both reduced species are present in solution; at 1335 nm the semiquinone and at 880 nm the dianion. The small peak at 1100 nm was assigned by Miller to the vibrational splitting observed in symmetrical anions.¹⁰ As the

potential is made more negative (-1600 mV) all the semiquinone is converted into the dianion (880 nm).

Figure IV.5. UV-Vis-NIR spectra of poly(aryl ether quinone) **13** under different applied voltages

A dark green color was observed on the working electrode when the semiquinone was present, and upon further reduction a blue color appeared indicating the presence of the diradical anion. This observation is in accordance with the literature indicating a green color for the semiquinone of pentacenediquinone **1**, and a blue color for the radical anion.¹¹ Upon reoxidation polymers **13** and **15** leave some residual NIR absorbance, but for the other two the reduction is fully reversible.

The values λ_{max} (nm) obtained for the semiquinone and diradical anions are presented in Table IV.2.

Table IV.2. Half - wave potentials and NIR peaks for the series of poly(aryl ether quinone)s^a

Polymer	E _{1/2} (mV)	Q ⁻ λ _{max} (nm)	Q ²⁻ λ _{max} (nm)
13	111, 563	1339, green	880, blue
14	159, 491	1339, green	888, blue
15	187, 579	1335, green	Not observed
16	Not available	1353, green	935, blue

Poly(aryl ether quinone)s **13-15** are similar in structure with pentacenediquinones **11a** and **11b**. Therefore, the spectroelectrochemical behaviour of polymers **13-15** should be similar with pentacenediquinones **11a** and **11b**. The semiquinone of pentacenediquinones **11a** and **11b** displays absorption at 1331 nm and the dianion at 880 nm. The semiquinone of polymers **13-15** displays NIR absorption around 1335 nm due to the presence of the ether group that has an electron-donating effect. The semiquinone of polymer **16** absorbs at 1353 nm due to the presence of an electron-withdrawing substituent (NO₂) that counterbalance the electron-donating effect of the ether group. The radical anion and dianion can be prepared *in situ* by reduction of the polymer films cast on ITO using LiClO₄ in DMF as supporting electrolyte. The color change is very visible, from red for the neutral form, to green for the semiquinone and blue for the dianion (Figure IV.6).

^a The study was performed in solution. Due to the difference in solubility between poly(aryl ether quinone)s it was impossible to prepare solutions of a known molar concentration.

Figure IV.6. Films of poly(aryl ether quinone) **15** on ITO:

neutral (a), semiquinone (b) and dianion (c)

One interesting finding is an unusual stability in air of the films that were reduced electrochemically on ITO. The films (Figure IV.6.b) can be handled in air without affecting the NIR properties. The NIR absorption was followed using UV–Vis–NIR spectroscopy and the peak position at 1330 nm and its intensity remained unchanged for months (Figure IV.7).

Figure IV.7. UV – Vis-NIR absorptions of the film prepared from the semiquinone of polymer **15**: (a) as prepared at – 800 mV, (b) after three weeks in air

IV.7. Conductivity

The Miller group investigated the conductivity of some semiquinone salts prepared electrochemically from four monoquinones and two pentacenediquinones. The salts were compressed into packed powders and investigated using a four probe method in an inert atmosphere to prevent the hydrolysis of the semiquinone salts to the corresponding quinones. The results are presented in the Table IV.3:¹²

Table IV.3. Conductivity of semiquinone salts

Compound	Metal (Semiquinone salt)	Conductivity: σ (S/cm)
Li^+	1
	Na^+	5×10^{-3}
	K^+	4×10^{-4}
	Me_4N^+	2×10^{-2}
Li^+	4×10^{-5}
Li^+	$< 10^{-5}$
Li^+	$< 10^{-5}$
Li^+	$< 10^{-5}$
Li^+	$< 10^{-5}$

All the monoquinone salts were insulators. The pentacenediquinone salts were the most conductive. For these salts, it was found that as the cation size increases, σ decreases in order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. The tetramethylammonium salt is rather conductive, in spite of the large size of the cation. These results demonstrate that conductivity is intrinsic to the pentacenediquinone radical anion and the crystal structure of semiquinone Me_4N^+ implies conductivity along the stacks of anions.¹² According to Miller it is unusual to have a good conductivity in a 1:1 salt without partial charge transfer between the ions. This phenomenon is probably due to the fact that there is one electron and two quinone moieties, resulting in a mixed valence species. The semiquinone has a low lying excited state, and in the solid this provides the opportunity for charge transfer from the half filled π^* orbital of one molecule to an empty but low lying π^* orbital on a neighbour in the

stack. Considering the short distance between anions in the stack, this mixing will probably lead to a band structure very effective in conduction.¹²

Since the Miller group has done quite intensive studies on the conductivity, we did not pursue our own study on the conductivity of the series of pentacenediquinones.

Thus, it is also expected for the polymers **13-16** to display some conductivity, although may be low due to the non-conjugated nature of the polymer and the poor packing of the quinone moiety.

Conductivity for polymers **13-16** was determined using a two-point probe measurement in air, in the dark and under light. The polymeric films on ITO were electrochemically reduced using Li^+ as a counter ion. The thickness of the films varied between 1.0 and 1.5 μm . The reduced films were coated with the gold–palladium electrode. The bulk conductivity was determined through the two electrode contacts (Figure IV.8).

Figure IV.8. Cell for conductivity measurements

The conductivity was calculated using the following equations:

$$R = U/I \quad (\Omega) \quad (8)$$

$$\rho = RA/t \quad (\Omega\text{cm}) \quad (9)$$

$$\sigma = 1/\rho \quad (\text{S/cm}) \quad (10)$$

where R is the electric resistance (Ω), U is the potential (V), I represents the intensity of the electric current (A), ρ is the resistivity (Ωcm), A represents the surface under the electrode (cm^2), t represents the thickness of the film (cm), and finally σ represents the conductivity (S/cm).

All the reduced polymers displayed conductivity between 10^{-5} and 10^{-6} S/cm. The conductivity values obtained for the poly(aryl ether quinone)s series are presented in Table IV.4. The values for the conductivity measured in the dark and under light do not differ.

Table IV.4. Conductivity values for poly(aryl ether - quinone)s **13-16**

Polymer	σ (S/cm), neutral	σ (S/cm), semiquinone
13	8.6×10^{-12}	6.3×10^{-5}
14	2.28×10^{-12}	2.3×10^{-5}
15	1.6×10^{-12}	5.93×10^{-5}
16	2.85×10^{-12}	1.6×10^{-6}

IV.8. Optical Attenuation

Optical attenuation is defined as a logarithmic relationship between the optical output power and the optical input power. It is related to the optical loss which can be expressed as:¹³

$$\alpha = (\log P_0 - \log P(L))/L \quad (\text{dB/km}) \quad (11)$$

where α represents the optical loss (dB/km), P(L) represents the optical power at the distance L from the input, and P_0 the optical power at the fiber input. In practice for optic fibers, it is highly desirable to minimize the optical loss. In the case of devices such as variable optical attenuators (VOA), the attenuation or optical loss is a desired process.

In the laboratory, to test the attenuating property of materials suitable for VOA applications, the equation (11) was modified into equation (12):¹²

$$\text{dB}/\mu\text{m} = 10(\log T_{\text{ox}} - \log T_{\text{red}})/\text{thickness} \quad (12)$$

where T_{ox} is the transmittance determined at the oxidation potential (maximum value on the graph), and T_{red} is the transmittance measured at the reduction potential (minimum value).

For the attenuation study, the polymeric films were cast on ITO glass which was used as the working electrode. Silver and a platinum electrodes were also used, with a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte (Figure IV.9). The pulse width chosen was 2 seconds and the values for T_{ox} were taken at the oxidation potential where all reduced species have been oxidized, and the values for T_{red} were obtained from the reduction potential which gives the most intense absorption in the NIR region. The results from the attenuation study are presented in Table IV.5.

Figure IV.9. Setup for attenuation measurement

Figure IV.10. Change in transmission at 1550 nm for the film of polymer **15** on ITO switched at 2 s

For example for compound **15**, when the film is in the reduced state (semiquinone) the transmittance decreases from 98.5 to 95.5 %. After a 2 seconds pulse width, the potential is switched to the oxidation potential and the transmittance value returns to 98.5% (Figure IV.10).

Table IV.5. Attenuation values for poly(aryl ether quinone)s **13-16**

Polymer	Attenuation [dB/ μm]	Thickness [nm]
13	0.03	505
14	0.024	41.5
15	0.4	306
16	0.747	49

The thickness of the polymeric films was determined by spectral ellipsometry. The films proved to be quite resistant to air displaying very good adhesion to the ITO substrate and not losing the attenuation value after 10 hours of switching (1800 cycles).

IV.9. Conclusion

A series of four poly(aryl ether quinone)s were prepared via nucleophilic aromatic substitution. The polymers were characterized mainly by infrared spectroscopy, differential scanning calorimetry and inherent viscosity. The polymers retain the NIR absorption observed for pentacenediquinones. The reduced films of poly(aryl ether quinone)s are stable in air for months and also display a conductivity of roughly 10^{-3} S/cm. Poly(aryl ether quinone)s also display optical attenuation, good adhesion to the ITO substrate and very good fatigue resistance.

IV.10. Experimental

Materials

Potassium carbonate, all bisphenols, tetrabutylammonium hexafluorophosphate, tetrabutylammonium perchlorate, and electrochemical grade *N,N*-dimethylformamide (DMF) were purchased from Aldrich and used as received. Sulfolene was distilled and dried over molecular sieves.

Methods

As presented in chapter III.4, cyclic voltammetry was performed using a BAS 3C stand, the spectro-electrochemical properties were investigated using an OTTLE cell, and the obtained response recorded using a UV–Vis-NIR Lambda 900 spectrophotometer. A solution of 0.1 M Bu_4NPF_6 in DMF was used as a supporting electrolyte. For the preparation of films, the polymeric solutions were filtered through a 2.5 μm filter and cast on the ITO substrate for the conductivity measurements. For the attenuation study the solutions were spin coated on the ITO. The resulted films were dried for 48 hours in an

oven under nitrogen at 40 °C. The thickness and indexes of refraction of the films were determined using a J.A. Woolam Co. Inc. VASE Spectral Elypsometer. The conductivity of the semiquinone films was determined using a Sigmatone box and a two point probe measurement. The attenuation study was performed using a BAS 3C stand and the response followed using a UV-Vis-NIR Lambda 900 spectrophotometer. A solution of 0.1 M Bu₄NPF₆ in acetonitrile was used as a supporting electrolyte. The films were switched between the oxidation and the reduction potentials using a pulse width of 2 seconds. The attenuation response was investigated for the 1300 nm window. Glass transition temperatures were measured on a Seiko DSC 220 at a heating rate of 10 °C per minute under nitrogen, and Infrared spectra were recorded on a Bomem Michelson 120 Fourier transform instrument.

General procedure for the synthesis of poly(aryl ether quinone)s

In a very dry three neck round bottomed flask equipped with magnetic stirring, argon inlet, Dean-Stark trap and reflux condenser were added 0.002 moles bisphenol, 0.003 moles K₂CO₃, 0.002 moles difluoropentacenediquinone, 25 mL toluene and 5 mL sulfolene. The mixture was heated at 120 °C for 2 hours until most of K₂CO₃ was consumed and a green color appeared. The temperature was raised to 150 °C and toluene distilled into the Dean-Stark trap. The reaction was allowed to proceed usually for eight hours. The mixture was cooled to room temperature and poured on ice. The solid was filtered by suction and dried in a vacuum oven at 100 °C for 24 hours. Yields varied between 80 and 100%.

Poly(aryl ether quinone) (13) 0.600 g (80 %) greenish solid. IR (KBr cm^{-1}): 1677 (C=O carbonyl), 1587 (C=C aromatic), 1507, 1487, 1364, 1322 – 1002 (C-O ether), 946, 921, 849, 724.

Poly(aryl ether quinone) (14) 0.400 g (80 %) dark brown solid. IR (KBr cm^{-1}): 1677 (C=O carbonyl), 1583 (C=C aromatic), 1507, 1487, 1364, 1322 – 1002 (C-O ether), 946, 921, 849, 724.

Poly(aryl ether quinone) (15) 1.200 g (100 %) purple solid. IR (KBr cm^{-1}): 1683 (C=O carbonyl), 1579 (C=C aromatic), 1517, 1487, 1353, 1324 – 1102 (C-O ether), 950, 911, 869, 720.

Poly(aryl ether quinone) (16) 1.400 g (100 %) dark purple solid. IR (KBr cm^{-1}): 1687 (C=O carbonyl), 1600 and 1555 (NO_2), 1580 (C=C aromatic), 1517, 1480, 1324, 1312 – 1002 (C-O ether), 936, 911, 839, 704.

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Chapter V. Synthesis and Characterization of Halogenated Pentacenes

For the past four decades, silicon and gallium arsenide semiconductors have been the backbone of the semiconductor industry. Recently, there has been a growing interest in “organic electronics”.^{1,2} Organic materials cannot compete with single-crystalline semiconductors which have charge carrier mobilities (μ) about three orders of magnitude higher than that of organic electronic materials. Also, such organic semiconductors are not suitable for applications that require very high switching speed.^{3,4} Table V.1 lists the mobility values of some organic materials in parallel with some well-known inorganic semiconductors.¹

Table V.1. Structures and mobilities of classes of organic and inorganic semiconductors¹

Semiconductor	Representative chemical structure	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Silicon	Silicon crystal	300 - 900
	Polysilicon	50 - 100
	Amorphous silicon	~ 1
Pentacene		~ 1
α,ω -dihexyl-sexithiophene		10^{-3}
α,ω -dihexyl-anthradi-thiophene		10^{-3}

In addition to their interesting electronic and optical properties, many of these organic thin-film materials possess good mechanical properties (flexibility and toughness) and can be processed using techniques familiar to the semiconductor and

printing industries, such as vacuum evaporation, solution casting, ink-jet printing and stamping.²

V.1. n – Type and p – Type Semiconductors

The electronic conductivity of a material (σ , conventional units are S/cm, equivalent to $\Omega^{-1}\text{cm}^{-1}$), represents the charge transported across a unit cross – sectional area, per second, per unit of applied field.⁵ Materials are divided into three broad categories of conductivity: insulators ($\sigma = 10^{-7}$ – 10^{-18} S/cm), semiconductors ($\sigma = 10^{-7}$ – 10^2 S/cm), and metallic conductors ($\sigma = 10^2$ – 10^{18} S/cm) (Figure V.1).⁶

Figure V.1. Conductivity values for various materials³

Conductivity of a solid state material requires that the electrons occupy partially filled orbitals, which is achieved by occupancy of the conduction band.⁵ For metals, the conduction and valence band overlap and therefore the conduction band can be readily occupied (Figure V.2).⁵

Figure V.2. Generation of bands in solids from atomic orbitals of isolated atoms⁵

For insulators, the band-gap is sufficiently large that electrons cannot be promoted from the valence band to conduction band. However, for semiconductors, the band-gap is not as large, and electrons can be moved into conduction band. The promotion of electrons leaves a positively charged vacancy in the valence, which is referred as a hole.⁵ These holes can be moved through the space by the transfer of an electron to the vacancy, therefore holes are considered to be mobile. Electrons can be excited to the conduction band either thermally or photochemically.

There is another method for generating charge carriers within a semiconductor known as doping. Doping involves the introduction of a group five element (e.g. P), or a group three element (e.g. Al) into a group four element (e.g. Si). Undoped semiconductors are referred to as intrinsic semiconductors.⁵ Doped semiconductors in

which the dominant charge carriers are electrons are referred to as n-type semiconductors, and those in which holes are the majority charge carriers are referred to as p-type semiconductors.⁵

In a similar way, organic semiconductors are divided into n-type and p-type semiconductors. For the p-type semiconductors, where the organic molecules would be considered electron donors, the charge carriers are holes. In Figure V.3 are presented some organic p-type semiconductors.⁷

Figure V.3. p-Type organic semiconductive polythiophenes

Electron-accepting organics are n-type and form channels of electrons. In Figure V.4 are presented some n-type organic semiconductors.^{8,9}

Figure V.4. n-Type organic semiconductors

The degree of mobility of charge carriers through organic materials is related to the presence of π - π orbital overlap to provide a route for carrier transport. Structural order in the material is also of great importance since it has a strong influence on the carrier mobility. For amorphous and microcrystalline samples, $\mu = 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, whereas for single crystals of aromatic compounds μ is typically $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the crystal axis direction with the maximum intermolecular π - π overlap. Even this value is three orders of magnitude lower than the mobility within typical inorganic semiconductors.^{5,6}

Band theory is used to describe electronic conduction in inorganic semiconductors and also in organic systems. For a molecular crystal, the valence band is formed by the combination of the highest occupied molecular orbitals (HOMO, π -orbitals), while the lowest unoccupied molecular orbitals (LUMO, π^* -orbitals) contribute to the conduction band. Theoretical calculations suggest that the band width (ΔW) is very narrow (about 0.01 – 0.1 eV) for most organic materials due to poor orbital overlapping between

neighbouring molecules, which is probably the main reason for the low mobility of charge carriers.⁶

The energy required to excite an electron directly from the valence band to the conduction band in the pure material is known as the band-gap (E_g).⁶ The presence of the carrier traps in the band-gap has the effect of reducing the number of available charge carriers.⁶ To have a good mobility, a molecular crystal must be free of all types of defects.

Among organic semiconductors, pentacene has received special attention, because so far it shows the best field-effect mobility in organic transistors ($1.5 \text{ cm}^2/\text{Vs}$) and an on/off current ratio greater than 10^8 . These values are very similar to those of amorphous hydrogenated silicon (field-effect mobility larger than $0.5 \text{ cm}^2/\text{Vs}$ and on/off current ratio greater than 10^8). Pentacene also displays both types of conductivity, n-type and p-type.^{7,8}

Pentacene consists of five aromatic rings fused together (Figure V.5), deep blue leaflets or needles sparingly soluble in organic solvents.¹⁰

Figure V.5. Pentacene

Pentacene is a relatively reactive molecule, the reactions usually take place in the 6,13 positions. Pentacene is susceptible to chlorination with PCl_5 and Diels-Alder cycloaddition with maleic anhydride, *p*-benzoquinone, and *p*-chloranil.

V.2. Synthesis of Pentacene and its Derivatives

The purpose of synthesizing halogenated pentacenes is to investigate the conductivity of such compounds using transistor templates and to see if the type of substituent and its position has an effect on conductivity and air stability. There are three major ways of preparing pentacene: cycloaddition of 1,4-benzoquinone to a corresponding diene followed by deoxygenation and dehydrogenation, Elbs pyrolysis followed by dehydrogenation, and Aldol condensation of o-phthalaldehyde with cyclohexane-1,4-dione followed by reduction with aluminum (Scheme V.1).^{7,10}

Scheme V.1. Synthetic routes to pentacene

However, the last two of these three methods don't seem suitable for making a halogenated pentacene, as the halogen groups are likely to be eliminated in the final steps. Starting from halogenated diquinones and using aluminum and cyclohexanol as a reducing agent¹⁰, a series of three halogenated pentacenes was obtained (Scheme V.2).

Scheme V.2. Synthesis of halogenated pentacenes from the corresponding diquinones

Other reduction systems like, hydroiodic acid or lithium aluminum hydride, are mentioned in the literature, but aluminum/cyclohexanol seems the best reducing agent for pentacenediquinones. The 65% yield for pentacene **17** was typically obtainable after 48 hours reduction. Using the halogenated pentacenediquinones as mixtures and as pure isomers, the difluoro- and dichloropentacenes (**18 a, b** and **19 a, b**) were prepared (Figure V.6). However, difluoropentacenediquinones were extremely difficult to reduce and the yields were low between 5 and 10%.

Figure V.6. Halogenated pentacenes prepared from the corresponding pentacenediquinones

V.3. Characterization of Halogenated Pentacenes

Characterization of substituted pentacenes was attempted using traditional methods for the characterization of organic compounds. Such methods include mass spectroscopy (MS) and infrared spectroscopy (IR). Unfortunately, nuclear magnetic resonance spectroscopy (NMR) was not used due to the poor solubility of such compounds.

Aromatic rings present C-H bands above 3000 cm^{-1} and also C-H out-of-plane stretching bands at $900 - 690\text{ cm}^{-1}$.¹² In Figure V.7. is presented the IR spectrum of 2,9-

dichloropentacene **19a**. The C=C stretch for **19a** can be observed between 1614 and 1440 cm^{-1} and also for all the halogenated pentacenes.

Figure V.7. IR spectrum of 2,9 – dichloropentacene **19a**

The aromatic compounds show very intense molecular ion peaks. In the case of aromatic compounds with chlorine atoms as substituents, the $M + 2$ peak becomes very significant. When two chlorine atoms are present, a quite distinct $M + 4$ peak, and a very intense $M+2$ peak should be observed.¹³ For dichloropentacene **19a** (Figure V.8.), the presence of a $M + 2$ peak of roughly 60% of the intensity of the molecular ion peak can be observed. The molecular ion peaks for the series of pentacenes are presented in Table V.2.

Table V.2. Molecular ion peaks for pentacenes 17-19

Compound	Molecular formula	HRMS molecular ion peak
17	$\text{C}_{22}\text{H}_{14}$	278.3526 calcd., 278.3598 found
18a and 18b	$\text{C}_{22}\text{H}_{14}\text{F}_2$	314 (MS m/e 100)
19a and 19b	$\text{C}_{22}\text{H}_{14}\text{Cl}_2$	346.0316 calcd., 346.0291 found

Figure V.8. Mass spectrum of 2,9-dichloropentacene **19a**

V.4. Electrical Characterization of Halogenated Pentacenes

Thin-film transistors (TFT) based on organic semiconductors are envisioned to be key components of plastic circuitry for use as display drivers in portable computers and pagers, and as memory elements in transaction cards and identification tags. Such transistors will by no means replace silicon in high performance, or high density devices, but are aimed instead at applications where flexibility, ease of fabrication and avoidance of high temperatures are of particular importance.^{1,2,5}

There are two geometries of organic transistors as shown in Figure V.9 (structures a and b).⁵ The structure (a) was used in this work to probe the electrical properties of halogenated pentacenes.

Figure V.9. TFT structures: (a) bottom contacts and (b) top contacts⁵

For 2,9-dichloropentacene **19a** the n and p-type behaviour were investigated using transistor cells. The films (Figure V.10) have been deposited in vacuum at 10^{-4} Pa and grown at 160 °C.

Figure V.10. AFM picture of the vapour deposited thin film of pentacene **19a**

For the investigation of the n-type behaviour an aluminum electrode was used, and for the study of the p-type behaviour a gold electrode was used. The resulting

transistor curves obtained in both case look different when compared to the pentacene curves. In both cases it seems that the saturation regime cannot be attained (Figure V.11). Evidently, these thin films do not show any transistor characteristics.

Figure V.11. I-V curves for 2,9-dichloropentacene **19a**: (a) n-type, and (b) p-type

One reason for this problem could be the poor quality of films obtained. Since the intermolecular overlaps in most organic crystals are small, it is important to grow large crystals without defects in order to obtain a better orbital overlap. These trials should be repeated in order to obtain realistic information about the field-effect mobility and on/off ratio of these novel compounds.

V.5. Conclusion

Starting from the corresponding pentacenediquinones, a series of five pentacenes were obtained using the aluminum/cyclohexanol reduction. The reduction requires 48 hours to complete and the yields vary between 5 and 65%. The structure of the compounds was confirmed using traditional methods for the characterization of organic

compounds. Due to the poor solubility of pentacenes in organic compounds, mass spectrometry and infrared spectroscopy were the methods of choice. Electrical characterization of halogenated pentacenes was attempted using transistor template. Due to poor film formation, both halogenated pentacenes failed to reach the saturation regime characteristic for organic transistors. In conclusion more investigations are necessary in order to establish a correlation between the substituents and the electron mobility of halogenated pentacenes.

V.6. Experimental

General Methods

Infrared spectra were recorded on a Bomem Michelson 120 Fourier transform instrument. Melting points have been determined on a Seiko DSC 220 at a heating rate of 10 °C per minute under nitrogen. Mass spectral analysis was performed at the University of Ottawa Mass Spectrometry Centre using a Kratos Concept 1H mass spectrometer. Pentacenes have been prepared as mixtures of isomers and also as pure isomers. All pentacenes have been purified by sublimation at 350 °C in a 10^{-5} Torr vacuum. The organic thin film transistors were made and measured by Professor Donghang Yan at the Changchun Institute of Applied Chemistry in China.

Materials

Chemicals were purchased from Aldrich. Cyclohexanol was freshly distilled and dried over molecular sieves prior to reduction. Aluminum dust was dried in an oven at 200 °C for 24 hours prior to use.

General procedure for reduction

In a round-bottomed flask containing 30 mL of dry cyclohexanol, were added with stirring 1 mL of CCl_4 , HgCl_2 (0.2 mmole), and aluminum dust (64 mmole) in small portions. The reaction mixture was heated at reflux for 15 hours until a green reaction mass formed. To the reaction mixture was then added 1.5 mmoles diquinone and the mixture heated to reflux for another 48 hours. Cyclohexanol was removed through vacuum distillation, and the resulted green mass was taken in aqueous HCl solution. The blue solid was filtered and stirred in 10% sodium dithionate solution to remove the unreacted quinone. The dark blue precipitate was extensively washed with concentrated hydrochloric acid, washed with methanol and stirred in toluene. The precipitate was dried in a vacuum oven at 110 °C for six hours. Yields usually varied between 10 and 65%.

Pentacene (17)

A blue solid 0.066g (16 %) was obtained. m.p.> 300 °C; IR (KBr cm^{-1}): 1498, 1443, 1296 (C=C aromatic), 1073, 957, 907, 731.9. HRMS calcd. for $\text{C}_{22}\text{H}_{14}$: 278.3526, found: 278.3598.

2,9 and 2,10–Difluoropentacene (18 a and b)

A blue solid 0.050g (10%) was obtained. m.p.> 300 °C; IR (KBr cm^{-1}): 1620, 1575, 1443, 1311, 1250 (C=C aromatic), 1130, 1043, 953, 907, 781.9. Low resolution MS (m/e) for $\text{C}_{22}\text{H}_{14}\text{F}_2$: 314 (100).

2,9-Dichloropentacene (19a)

A blue solid 0.250g (60 %) was obtained. m.p.= 350 °C; IR (KBr cm^{-1}): 1619, 1585, 1440, 1301, 1270 (C=C aromatic), 1129, 1060, 933, 907, 791.9. HRMS calcd. for $\text{C}_{22}\text{H}_{14}\text{Cl}_2$: 346.0316, found: 346.0291.

2,10-Dichloropentacene (19b)

A blue solid 0.166g (40%) was obtained. m.p.= 360 °C; IR (KBr cm^{-1}): 1629, 1580, 1460, 1321, 1270 (C=C aromatic), 1109, 1070, 933, 907, 791.9. HRMS calcd. for $\text{C}_{22}\text{H}_{14}\text{Cl}_2$: 346.0291, found: 346.0291.

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Summary and Conclusions

Starting from the classical well known pentacenediquinone, a series of twelve substituted pentacenediquinones were synthesized. The purpose behind this work was to investigate the NIR absorbance of the semiquinone form. All compounds displayed NIR absorbance in the reduced form in the three telecom windows (800, 1300 and 1550 nm). This study allowed establishment of a correlation between the type, number, and position of substituents and the maximum of absorbance in the NIR region, hence demonstrating the hypothesis stated in the introductory chapter.

Fluorinated pentacenediquinones were used for the preparation of a series of four electroactive polymers. The preparation of the polymers was necessary in order to investigate the NIR activity and the attenuation in solid state because this is very hard to achieve with small molecules since they have poor adhesion to the ITO substrate. The polymeric films proved to be switch resistant and displayed the same attenuation value after ten hours of testing. The films in the reduced form are electrochromic and showed an increase in conductivity from 10^{-12} S/cm to 10^{-5} S/cm that places them in the class of n-type semiconductors due to the doping effect of the lithium counter ion.

Halogenated pentacenediquinones were also reduced to pentacenes. Unfortunately, the studies done for halogenated pentacenes using transistor templates were inconclusive. Therefore, it is very hard to establish a correlation between the substituents, conductivity and air stability.

Future work should focus on the structural modification of pentacene in order to achieve good electron mobility and air stability, and also on the preparation and investigation of heterocyclic pentacenes such as thiophenepentacenes. It would also be

interesting to look at the effect of the doping agent on the conductivity value for the quinone polymers. Also a prototype attenuation device could be prepared using poly(aryl ether quinone)s.

This thesis research did not provide a new technology for the telecom or semiconductor industry, but has opened a new research direction and may have provided a source of inspiration for the design of novel molecules in the future.