



BRNO UNIVERSITY OF TECHNOLOGY

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ÚSTAV CHEMIE A TECHNOLOGIE OCHRANY ŽIVOTNÍHO PROSTŘEDÍ

MODIFICATION OF ORGANIC HIGH PERFORMANCE PIGMENTS FOR APPLICATIONS IN ORGANIC ELECTRONICS

MODIFIKACE ORGANICKÝCH VYSOCE VÝKONNÝCH PIGMENTŮ PRO APLIKACE
V ORGANICKÉ ELEKTRONICE

SUMMARY OF DOCTORAL THESIS

TEZE DIZERTAČNÍ PRÁCE

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BRNO 2020

ABSTRACT

The doctoral thesis deals with the study, synthesis and chemical derivatization of molecules belonging to the group of organic high-performance pigments and their potential application in the fields of organic electronics. The theoretical part of the work is focused on the latest trends in the area mentioned above, both from the application potential of specific derivatives and in terms of synthetic possibilities and their structural derivatization. The experimental part describes in detail the preparation of a wide range of intermediates and final products, including derivatives of diketopyrrolopyrroles (DPP), benzodifuranone (BDF), epindolidione (EP), naphthyridinedione (NTD) and thiophene-based polymer (PT). A total of 103 molecules were synthesized, of which 49 were final products, and 27 of them were completely novel, as yet unpublished. Herein, the main motive for the derivatization of pigment molecules is the incorporation of bulky adamantyl substituents into the resulting derivative structures. In the next part of the work, individual chemical modifications leading to the final products are discussed in more detail. In the series of *N,N'*-; *N,O'*- and *O,O'*-substituted DPP derivatives, the influence of both the alkyl chains' character and binding position in the DPP molecule on the selectivity of the reaction, the thermal and optical properties of the resulting derivatives is comprehensively described.

ABSTRAKT

Dizertační práce pojednává o studiu, syntéze a chemické derivatizaci molekul spadajících do skupiny organických vysoce výkonných pigmentů a jejich potenciálním uplatnění v oblastech organické elektroniky. Teoretická část práce je zaměřena na nejnovější trendy v dané oblasti, a to jak z aplikačního potenciálu konkrétních derivátů, tak z pohledu syntetických možností a jejich strukturálních derivatizací. V experimentální části je pak podrobně popsána příprava pestré škály intermediátů a výsledných produktů, zahrnujících deriváty diketopyrrolopyrrolů (DPP), benzodifuranonu (BDF), epindolidionu (EP), naphthyridinedionu (NTD) a polymeru na bázi thiofenu (PT). Celkově bylo nasyntetizováno 103 molekul, přičemž 49 tvořily výsledné produkty, z nichž 27 bylo zcela nových, dosud nepublikovaných. Hlavním motivem derivatizace molekul pigmentů je zde inkorporace derivátů adamantanu do finálních struktur. V další části práce jsou blíže diskutovány jednotlivé chemické modifikace vedoucí k výsledným produktům. Na sérii *N,N'*-; *N,O'*- a *O,O'*-substituovaných derivátů DPP je popsána komplexní studie vlivu charakteru alkylových řetězců a také pozice jejich navázání v molekule DPP, a to nejen na selektivitu reakce, ale rovněž na optické i termické vlastnosti syntetizovaných produktů.

KEYWORDS

Organic electronics, Pigment, Diketopyrrolopyrrole, Benzodifuranone, Epindolidione, Naphthyridinedione, Alkylation, Adamantane, Adamantyl, Asymmetric substitution

KLÍČOVÁ SLOVA

Organická elektronika, Pigment, Diketopyrrolopyrrol, Benzodifuranon, Epindolidion, Naphthyridinedion, Alkylace, Adamantan, Adamantyl, Asymetrická substituce

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1 OBJECTIVES OF THE DOCTORAL THESIS

The objectives of this doctoral thesis are:

- Write the review on organic high-performance pigments and related molecules and their application in the fields of organic electronics.
- Write the review on synthetic possibilities of derivatization of appropriate organic pigments and related molecules.
- Prepare and characterize a diverse range of novel original derivatives of organic pigments and related molecules with emphasis on the incorporation of adamantyl side chains into their structures.
- Prepare and characterize a completely novel, as yet undescribed thiophene analogue of a benzodifuranone derivative (BDF).
- Prepare and characterize an original fluorinated polymer based on thiophene with significantly prolonged π -conjugation of the monomer.
- Perform a comprehensive study of the influence of adamantyl side chains on the resulting properties of the selected series of alkylated DPP derivatives.

2 INTRODUCTION

Nowadays, electricity is an essential part of the daily life of most of the world's population. With the growing population of the Earth and the ever-increasing number of new technologies and their integration into the everyday life of present and future generations, the need for electricity continues to increase enormously. To meet the demand for this energy source in the future and to continue to take electricity for granted, as it is nowadays, really high demands are placed on developing new and increasingly efficient technologies that can produce electricity. Indeed, the research and development of technologies involved in generating net electricity are expanding significantly, and further growth is also expected in the coming decades, as confirmed by the graphs in **Figure 1** conducted by the independent statistical and analytical company U.S. Energy Information Administration (EIA)¹. Significant growth in net electricity production is predicted especially for countries that are not part of the Organization of Economic Cooperation and Development (non-OECD) with an average increase of 2.3% per year from 2018 to 2050, compared with 1.0% per year in OECD countries (**1A, Figure 1**). This increase is necessary because of the expected growth in electricity consumption in all sectors, including industry, residential, commercial, transportation etc. (**1B, Figure 1**).

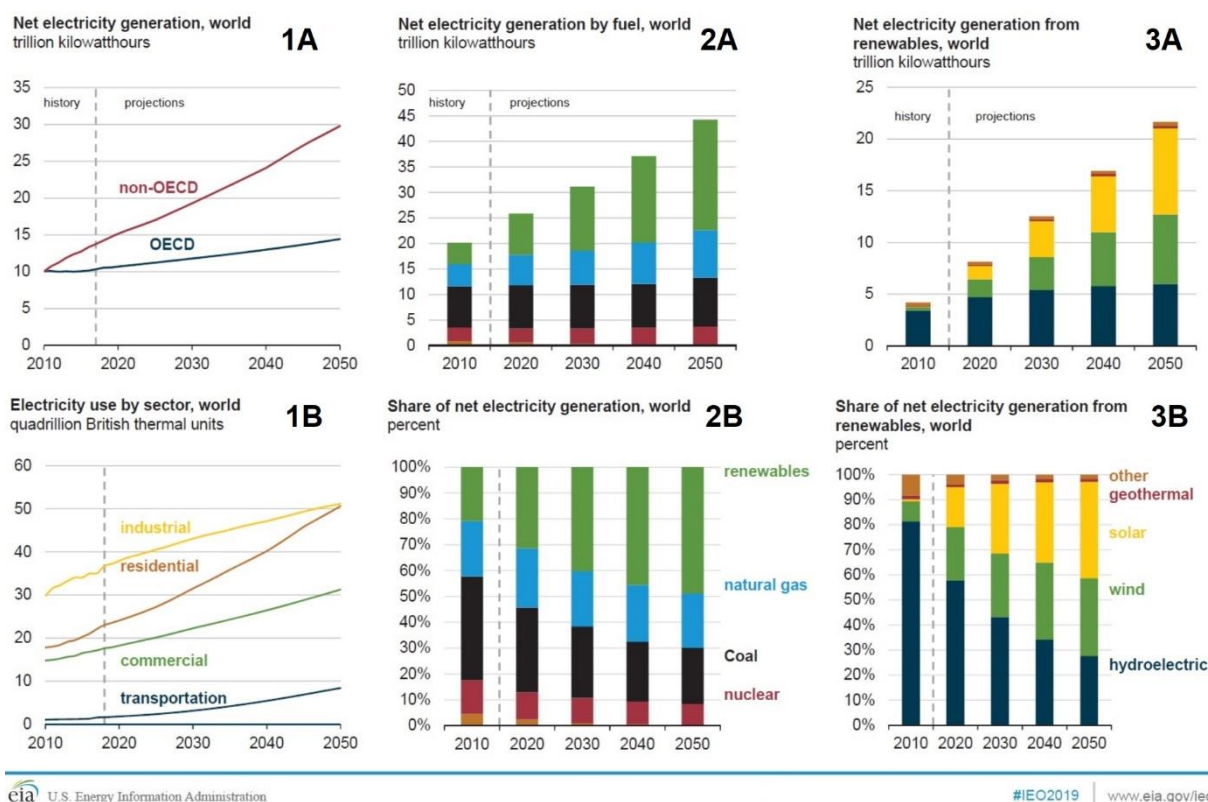


Figure 1: Statistic graphs describing development of net electricity generation and consumption by sector (1A–B), including distribution of energy sources by fuel (2A–B) and detailed analysis of renewable energy sources (3A–B) during period 2010–2050¹.

It is clear from the **2A–B** graphs in **Figure 1** that the development of new technologies for net electricity generation is focused primarily on renewable sources, which are the fastest-growing source of electricity generation during the 2018 to 2050 period, rising by an average of 3.6% per year. Technological improvements and government incentives in many countries support their increased use, which is the main reason for the expected development. Based on predictions, renewable energy sources will surpass coal as the primary source of electricity generation in 2025 and by 2050 renewables will account for almost half of the world's total electricity generation (**2B, Figure 1**)¹.

Upon closer analysis of the share of individual areas of renewable energy sources shows that currently, the dominant hydropower source expects only modest growth, which predicts a fall in the share of electricity generation from 62% in 2018 to only 28% in 2050. On the contrary, among renewable energy sources, electricity generation from solar resources is expected to grow dramatically between 2018 and 2050, reaching 8.3 trillion kilowatt-hours (kWh), as show **3A–B** graphs in **Figure 1**. The main advantage of solar energy is that this technology becomes more cost-competitive and is supported by government policies in many countries. Moreover, sunlight produces about ten thousand times more energy than the current global energy consumption, which is why the sun is considered one of the best and most affordable renewable energy sources. Therefore, solar energy will account for almost 40% of total renewables generation by 2050¹.

Nowadays, still dominating crystalline silicon photovoltaic cells have been on the market for over 40 years and have probably already reached their technological and performance peaks². Moreover, their production and disposal are considered uneconomical and very environmentally harmful. In the future, their use can be expected to decrease and, on the contrary, the use of organic solar cells (OSCs)³ and related hybrid materials (perovskite-based solar cells)⁴ are expected to increase, which should remove the previously mentioned disadvantages of silicon solar panels². Branch of the industry dealing with these issues is called organic photovoltaics (OPV), which belongs to a huge industrial area known as printed, organic and flexible electronics.

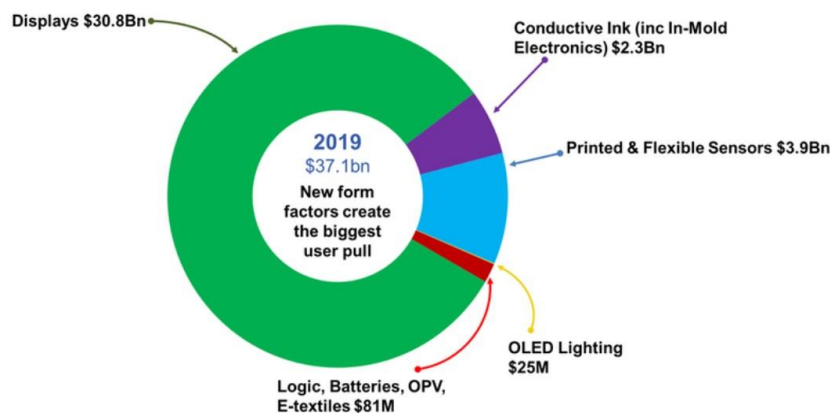


Figure 2: Market snapshot for printed, organic and flexible electronics in 2019⁹

In addition to the materials mentioned above and technologies involved in electricity generation, one of the main objectives of 21st-century research of organic electronics is the development of advanced materials that can also use this energy most effectively in modern electronic devices. There are also high demands on production costs and environmental impact of these materials, including constant miniaturization of components and meeting the growing requirements on their flexibility⁵. Thus, much effort has been put into developing narrow-band gap organic molecules, belonging to the category of semiconductors, that meet all these conditions much more easily than devices based on inorganic materials^{2,6,7}.

Organic electronics has been one of the most evolving disciplines of advanced material science and chemistry over the last 30 years⁸. In the past decade, a number of novel organic semiconductors have been developed and used in a wide range of organic and printed electronics fields, which are now experiencing a massive boom on the market and are currently among the most subsidized areas of science, and so it should be in the years to come. According to IDTechEx Research, the total market for printed, flexible and organic electronics will grow from \$37.1 billion for 2019 to \$41.2 billion in 2020 and to staggering \$74 billion in 2030⁹. As shown in the graph in **Figure 2**, the majority of this market today are displays based on organic light-emitting diodes (OLED)¹⁰, followed by printed sensors¹¹ and printed conductive inks¹² used predominately for photovoltaics. On the contrary, there are plenty of devices forming smaller segments, but with powerful growth potential, such as organic field-effect transistors (OFET)¹³, organic solar cells (OSC)¹⁴, biosensors¹⁵ etc.

My present research deals with the current trends and the latest knowledge in the field of organic high-performance pigments and structurally related molecules from the perspective of their potential applications in organic electronics. My work and research are focused primarily on small organic molecules, although polymeric materials based on pigments and related molecules are also the marginally aim of interest in my research. Nevertheless, the undisputed and very significant advantage of small molecules compared to polymers is their monodispersity, a well-defined molecular structure and therefore more predictable properties, easier preparation and subsequent purification or modification of their structure¹⁶. The chemical derivatization of the molecules allows practically unlimited possibilities to optimize the required parameters, which is the main objective of my research.

3 THEORETICAL PART

3.1 ORGANIC ELECTRONICS AND PHOTONICS

Organic electronics is currently a dynamically developing multidisciplinary modern branch of the electronics industry, using the interconnected knowledge of electronics, photonics, organic synthesis, material engineering, biotechnology and nanotechnology and many other disciplines. A crucial breakthrough in this area occurred in 1977 when polyacetylene was first prepared as an electrically conductive organic polymer¹⁷. In 2000, the Nobel Prize for Chemistry was awarded to three scientists Heeger, MacDiarmid and Shirakawa for this important discovery¹⁸.

Interest in the organic electronics industry is steadily increasing, resulting in an ever-growing number of investments in research and construction of new production lines, which are gradually becoming a priority for the world's leading companies in this field⁹, such as BASF, LG Display, Novaled GmbH, Samsung Display, Sony Corporation etc.¹⁹ Therefore, it can be expected that this progressive area of electronics will affect virtually all economic sectors in the future.

Application area of photonics deals with the use of light to generate energy, transmit or detect information. From a different perspective, photonics is a technology for generating and utilizing light and many other forms of radiant energy whose quantum unit is a photon²⁰. The related modern area called organic photonics deals with the above-mentioned light processes exhibiting in optical organic materials²¹. Currently, very interesting applications of organic photonics are, e.g. space technology²², biomedicine²³, alternate energy²⁴, information technology²³, laser technology²⁵, etc. The group of materials generally applicable in the field of organic photonics belongs to a large group of organic semiconductors²¹.

3.2 ORGANIC MATERIALS FOR ELECTRONICS

The basic building block of organic materials is a carbon atom, which forms single (σ -bond), double (σ -bond + π -bond) or triple (σ -bond + 2 π -bonds) bonds with other carbon atoms. There is a total of 4 electrons in the valence band of the carbon atom, in the ground state 2 in orbital 2s and one in orbital 2p_x and one in 2p_y. Due to the very small energy difference between fully occupied 2s orbital and unoccupied 2p_z, one electron is easily transferred among them, thus creating an excited state of the carbon atom, containing 4 unpaired electrons in its valence band^{26–28}.

The key prerequisite for the use of materials in the field of electronics is its ability to participate in charge transfer. To be able to perform this, the presence of a conjugated system of single and double bonds between carbon atoms and the presence of free charge carriers is the necessary structural parameter^{17,29}.

The formation of a conjugated double bonds system results in sp² hybridization of the carbon atoms, where the 2s orbital is mixed with two of the three available 2p orbitals (denoted as 2p_x and 2p_y). Thus it forms the trigonal planar molecular geometry. The carbon atom is placed in the centre, and triangle tops are formed by

hybridized orbitals with unpaired electrons, which are participating in the creation of a total of three σ -bonds. The remaining $2p_z$ orbitals containing the unpaired electrons involved in the π -bonds formation are placed perpendicular to the plane of the triangle^{26–28}. In structures containing conjugated double bonds system, π -bonds are spread over the structure, and therefore, π -electrons are delocalized over the whole skeleton of the molecule²⁸. Their free mobility then allows these molecules to participate in charge transfer³⁰. The described phenomenon is shown schematically in **Figure 3**.

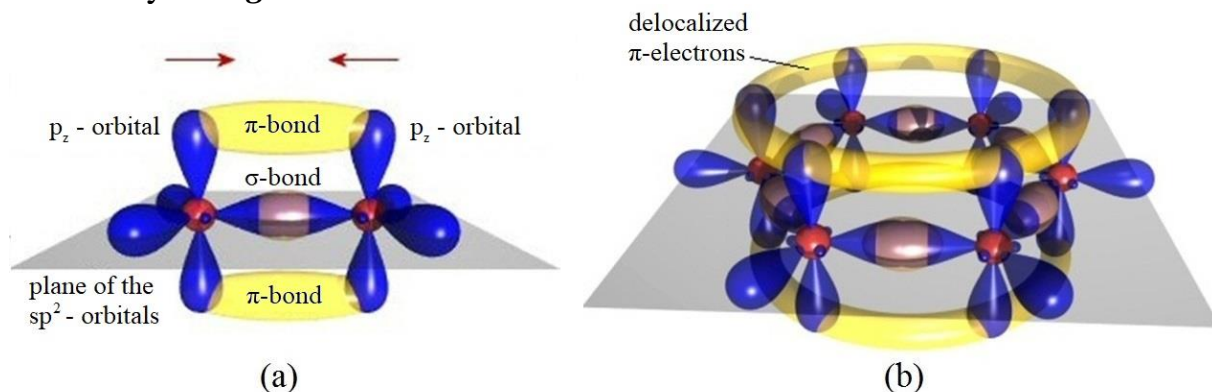


Figure 3: Formation of π -bonds in the ethene molecule (a) and the benzene molecule (b)

For solid-state crystalline materials applies the band theory, which explains how the atoms in the crystal lattice overlap their orbitals, describes the states of electrons and forming of discrete energy bands^{31,32}. The valence band is the last band of the electron shell containing electrons in the ground state and is therefore responsible for the formation of chemical bonds, as was discussed above. Band enabling charge transfer is called the conduction band, and it is the first unoccupied electron band in the ground state. In the case of materials known as conductors (typically metals), these two bands are in contact, respectively overlapped, and these materials are theoretically able to participate in charge transfer without any supply of energy. On the contrary, in the case of semiconductors and insulators, the valence and conduction bands are separated by a band gap, which is an energy range where no electron states can exist based on the quantisation of energy. Electrons located in the valence band can pass into the conduction band if they overcome the energy barrier, which is given by the width of the band gap.

In the case of organic semiconductors, the band gap energy denotes the energy distinction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which are the analogues to the valence and conduction bands of the above-discussed inorganic crystalline semiconductors. Therefore, the control of HOMO–LUMO energy gap of π -conjugated systems, and hence of the band gap of the corresponding materials, is a crucial task for the organic semiconductor designing. Moreover, the presence of the band gap allows organic semiconductors to absorb light radiation, which extends the application potential of these materials^{30,33}.

Organic substances suitable for applications in organic electronics can be divided into two fundamental groups: narrow band gap low molecular weight organic compounds (usually called “small molecules”)³⁴ and polymers³⁵. The first mentioned group includes substances having a relative molecular weight in the order of tens to a maximum of hundreds of g mol^{-1} , while polymers are compounds possessing a relative molecular weight typically in thousands of g mol^{-1} and a key parameter affecting their properties is the polydispersity.

High-performance organic pigments are a fairly wide range of substances, with excellent intense colouring, high stability against temperature and surrounding physical phenomena. They are normally used for dyeing plastics and synthetic fibres; many of them are also included in surface coatings such as varnishes and inks³⁶. A number of organic pigments are commonly found in nature, such as indigo in a plant of the same name. In most cases, however, their large-scale industrial production is also possible, which greatly contributes to the abundant expansion of pigments and the ability to find applications in other industries³⁶.

Over several years of research, it has been found that many molecules of organic pigments are able to participate in the transfer of charge carriers due to the presence of the delocalized π -electron system, thus rapidly incorporating them into a class of substances called semiconductors. This discovery sparked a rocket growth of interest in organic pigments in the areas of organic electronics, and these derivatives are still the focus of many research teams around the world^{8,10,13–15,36}.

As already mentioned, small molecules of organic pigments generally allow for a very diverse range of chemical derivatization, thereby targeting and designing the desired properties¹⁶. Organic semiconductors can be categorically divided into *n*-type, *p*-type, and ambipolar, depending on whether they mediate the transport of electrons, holes, or both types of charge carriers. The following chapters will deal with the groups of substances involved in my research, i.e. selected important organic high-performance pigments, related π -conjugated molecules and their derivatization.

3.2.1 Diketopyrrolopyrroles (DPPs)

The main backbone of the diketopyrrolopyrrole (DPP, **1**) molecule forms a bicyclic dilactam of aromatic character, with the systematic name 2,5-dihydropyrrolo[4,3-*c*]pyrrolo-1,4-dione (**Figure 4**). The DPP molecule was first prepared in 1974³⁷, and shortly thereafter it became widely used as a pigment in inks, as well as in paints for coating purposes, and its potential for applications in organic electronics has been hidden for many years. The first solution-processable DPP-based semiconductors for OPV³⁸ and OFET³⁹ devices was synthesized and reported only in 2008, and it has since been a key fragment of several thousands of scientific papers focused primarily on organic electronics^{40,41}. With this discovery, the DPP molecule has indeed been recognized as a promising conjugated building unit to construct high-performance semiconducting materials for various electronic

devices. Moreover, the facile synthesis of the DPP and the possibility of its easy chemical derivatization, which allows tuning the optoelectronic properties to match the requirements for the corresponding devices, are the key benefits for their widespread use⁴¹.

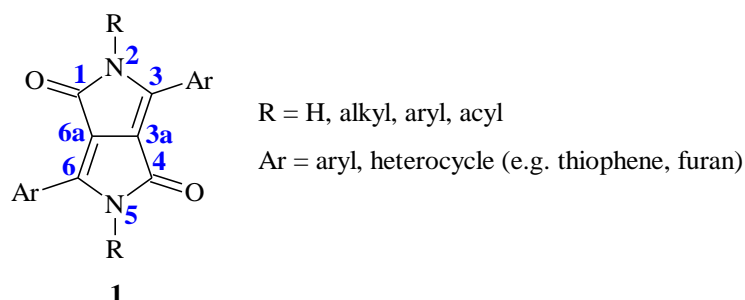
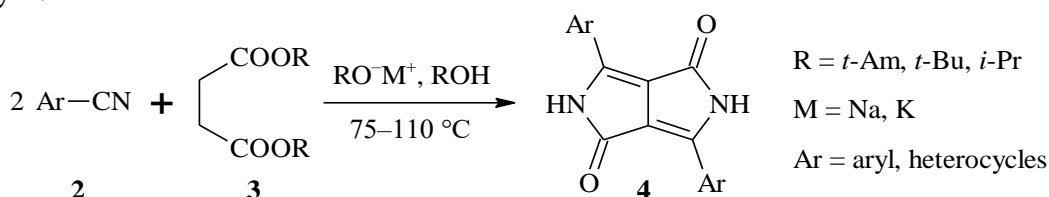


Figure 4: The general skeleton of the DPP molecule (**1**) with atom numbering

Many approaches to preparing the DPP molecule (**4**) have been developed since its discovery in the early 1970s by Farnum et al.³⁷, and all of them are clearly described in review from Gryko et al.⁴² By far the most used method is a condensation of nitrile-derivatives (**2**) with succinic acid esters (**3**, *Scheme 1*), which are substrates derived by retrosynthetic analysis from the *Reformatsky* mechanism of the DPP molecule synthesis, developed in the early 1980s by the Ciba-Geigy AG company⁴³.



Scheme 1: Succinic method to preparation the DPP molecule (**4**)⁴³

The DPP skeleton contains several reactive functional groups, which provides a varied range of substitution reactions, both electrophilic and nucleophilic⁴⁴, as shown in *Figure 5*.

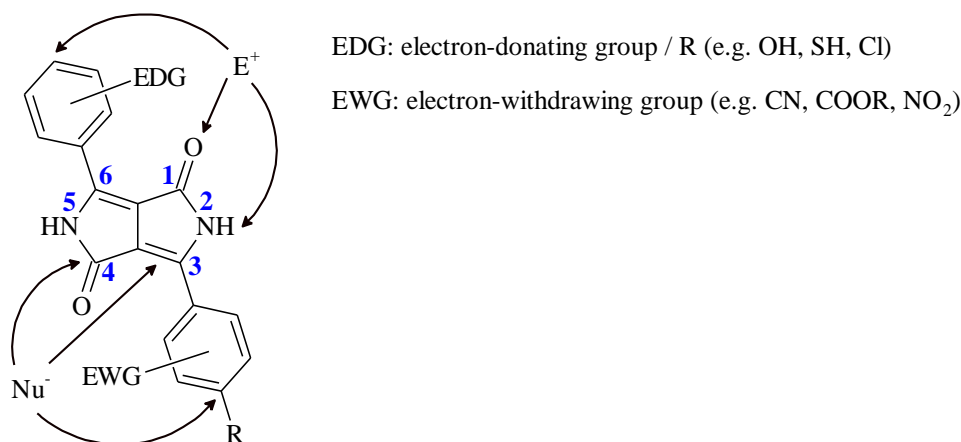


Figure 5: Reactivity of the DPP skeleton with phenyl side-chains⁴⁴

Over the last several decades, synthetic modifications of the DPPs have been able to significantly improve the performance of electronic devices based on these derivatives. Therefore, the DPP molecule has proven to be a successful building block for constructing high-performance functional materials that are suitable for a wide range of applications in the electronic industry as already mentioned⁴¹. However, interest in derivatives based on the DPP molecule has so far not slackened, and even today, an average of about 150 scientific publications and more than 200 patents dealing with these organic pigments are recorded annually⁴².

3.2.2 Benzodifuranones (BDFs)

The benzodifuranone (BDF, **5**) molecule contains 2 lactone groups in its structure and forms a systematic name furo[2,3-*f*][1]benzofuran-2,6-dione (**Figure 6**).

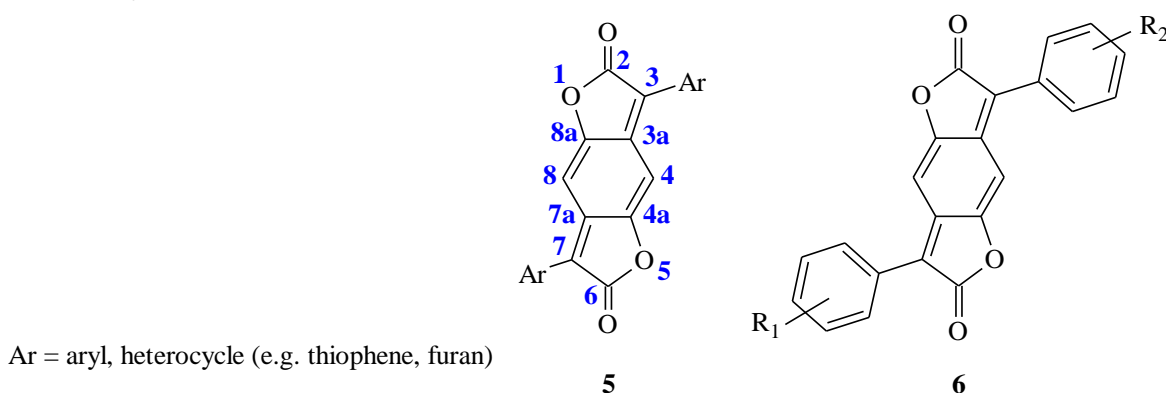
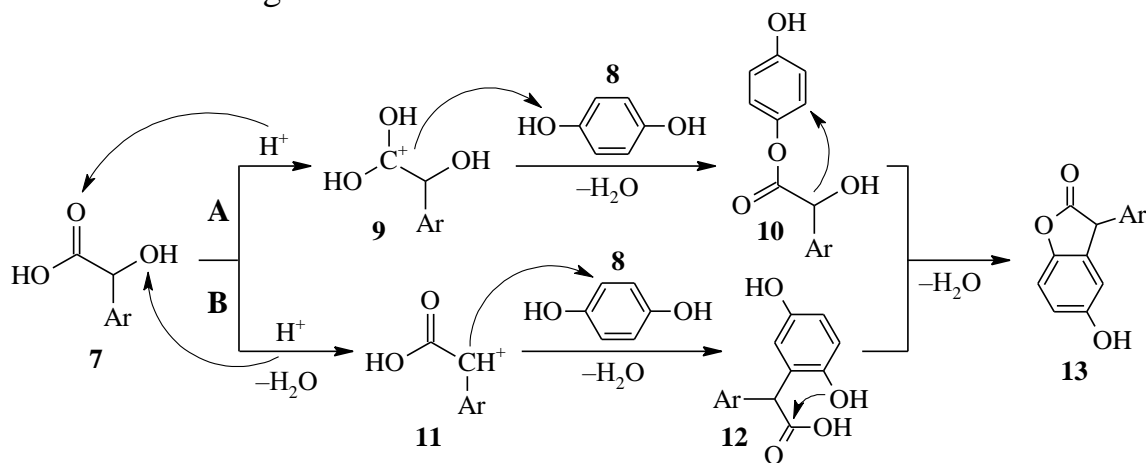


Figure 6: The general skeleton of the BDF molecule (**5**) with atom numbering and derivative **6**

BDF derivatives rank among commercial, industrial dyes, as well as DPP derivatives. Since the 1990s, BDFs have been widely used, for example, for dyeing polyester fibres in the textile industry^{45,46} and they are gradually replacing the anthraquinone and azo dyes used so far⁴⁷. BDF derivatives excel further possibility of producing a wide spectrum of colouring, which is readily modifiable by the substituents R_1 and R_2 (**6**, **Figure 6**), whose character significantly influences the radiation absorption of certain wavelengths⁴⁷.

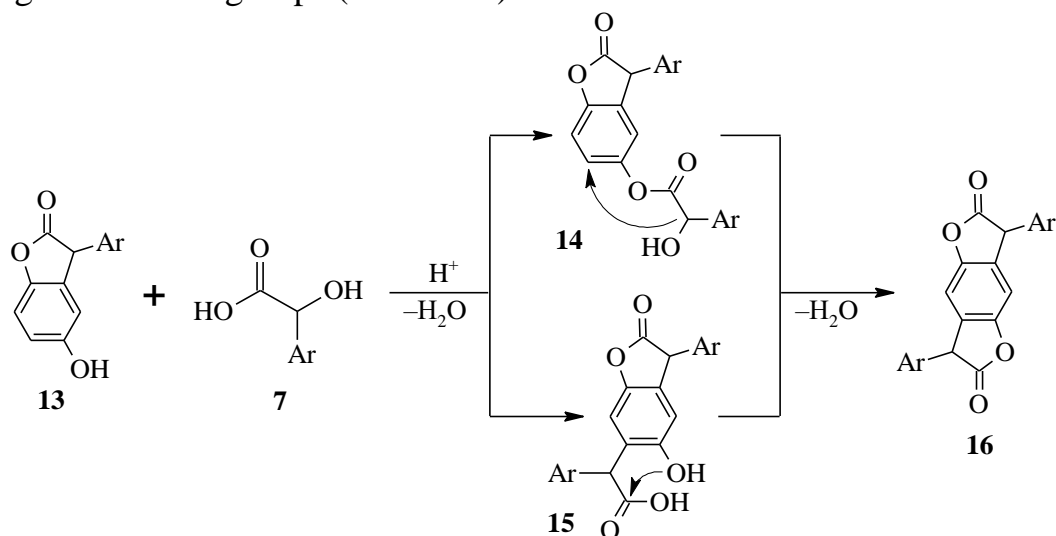
The benzodifuranone (BDF, **5**) molecule was firstly prepared in the early 1980s⁴⁶. The synthesis of BDF derivative occurs in several synthetic steps, where the key starting materials are derivatives of α -hydroxy acids (AHAs, **7**)⁴⁸. Before the formation of the resultant BDF skeleton, the mono-condensation to the benzofuranone derivative (**13**) first occurs. In the literature, two most probable mechanisms are described (**Scheme 2**). The first one (**A**) assumes acid-catalysed esterification (so-called *Fischer esterification*), where the nucleophilic oxygen atom of the hydroquinone (**8**) attacks the carboxylic carbon activated by the proton transfer from acid catalyst to the carbonyl oxygen of the AHA molecule (**9**). Then, the resulting ester (**10**) undergoes intramolecular cyclization to form the molecule **13**, containing lactone functional group. The second one (**B**) assumes the

protonation of an α -hydroxy group of the AHA molecule, followed by its dehydration to form the carbocation (**11**), which reacts *via* electrophilic substitution with hydroquinone (**8**) to intermediate **12**. Subsequent intramolecular cyclization of **12** leads to the resulting molecule **13**^{48,49}.



Scheme 2: Formation of benzofuranone mono-condensate (**13**) – two possible mechanisms^{48,49}

After the mono-condensate **13** is formed, it reacts with another molecule of AHA (**7**) by one of the mechanisms described above to intermediates **14** or **15**. Their subsequent intramolecular cyclization provides the double-condensate (**16**), containing two lactone groups (**Scheme 3**)⁵⁰.

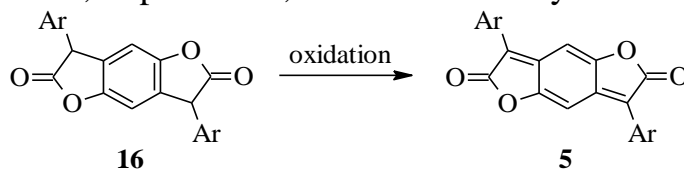


Scheme 3: Formation of the final benzofuranone double-condensate (**16**) – two possible mechanisms

The formation of the resulting double-condensate (**16**) has two options – (I) through the preparation of mono-condensate (**13**) first and subsequently the second cyclization to the final molecule **16**; (II) *via* direct double-condensation to the molecule **16**. The great benefit of approach (I) is the ability to prepare both symmetrical and asymmetrical BDF derivatives, whereas approach (II) provides only symmetrical BDFs⁵⁰.

The last synthetic step to the final BDF molecule is the oxidation of the derivative **16** (**Scheme 4**). For this purpose, a wide variety of solvents and oxidizing agents are

used. The most commonly used solvents are 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, acetic acid, sulphuric acid etc. On the other hand, typically used oxidizing agents are *m*-chloroperbenzoic acid, *p*-toluenesulfonic acid, nitrobenzene, hydrogen peroxide, potassium or ammonium persulfate, chloranil etc. The use of an oxidizing agent is derived, in particular, from its solubility in the used solvent⁵⁰.



Scheme 4: Oxidation of the di-condensate (**16**) to the final BDF molecule

3.2.3 Derivatives of indigo (ID) and isoindigo (IID)

Indigo is one of the world's most well known and most commonly used natural pigments. Its first confirmed use is dated to 6 000 years ago for cotton dyeing⁵¹. It is an intensely blue substance, originally obtained from leaves of the plant of the same name. Synthetic indigo was first prepared in 1870 and gradually replaced the natural indigo during the 19th century. Today its annual global consumption reaches several thousand tons, and it is mainly used in the textile industry⁵². The structures of the indigo (ID, **17**) molecule and its congener isoindigo (IID, **18**) are shown in the following **Figure 7**.

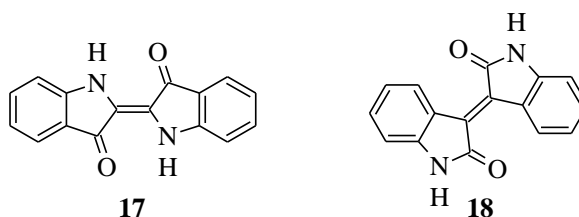
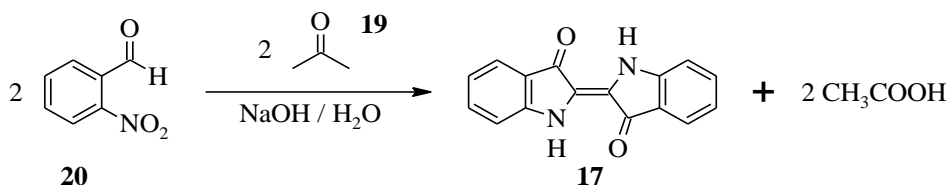


Figure 7: The general skeleton of the indigo (**17**) and isoindigo (**18**) molecules

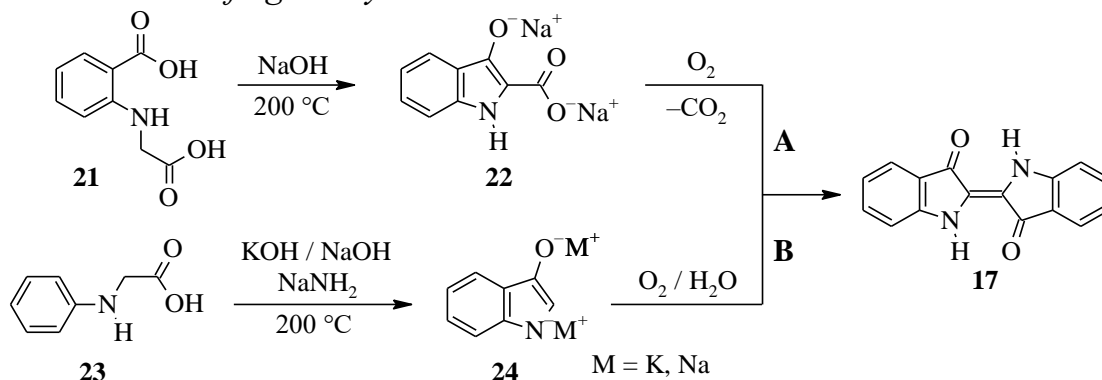
The synthesis of the ID molecule has several ways⁵³. The first one – *Baeyer-Drewsen synthesis* – dates back to 1882 and is based on the aldol condensation of acetone (**19**) with *o*-nitrobenzaldehyde (**20**) in the presence of sodium hydroxide solution, followed by cyclization and oxidative dimerization to the resulting molecule of ID (**17**), as shown in the following **Scheme 5**. However, this synthetic pathway is still used on the laboratory scale⁵⁴.



Scheme 5: The Baeyer–Drewsen synthesis of the indigo molecule (**17**)

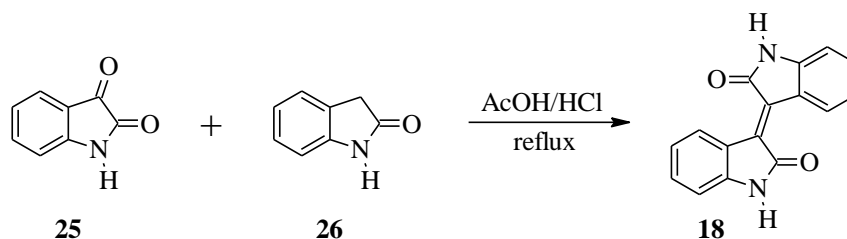
Second synthetic pathway called *Heumann's* dating from 1897 uses *N*-(2-carboxyphenyl) glycine (**21**), which is heated to 200 °C in an inert atmosphere with

sodium hydroxide as a base to form indoxyl-2-carboxylate (**22**), followed its decarboxylation to give indoxyl, which is subsequently oxidized in air to the ID molecule **17** (A, *Scheme 6*)⁵⁵. Last important method is *Pfleger's synthesis* from 1901, where *N*-phenylglycine (**23**) reacts with a molten mixture of potassium and sodium hydroxide and sodium amide to form the indoxyl molecule as the stable dialkali-metal salt (**24**), which is then oxidized in air to the resulting ID molecule **17** (B, *Scheme 6*)⁵⁶. Currently, these two methods for preparing the ID molecule are commonly used for industrial mass production. While the *Heumann's* pathway is simpler than the *Pfleger's*, however, the starting material **21** is more expensive than the molecule **23** for *Pfleger's synthesis*⁵³.



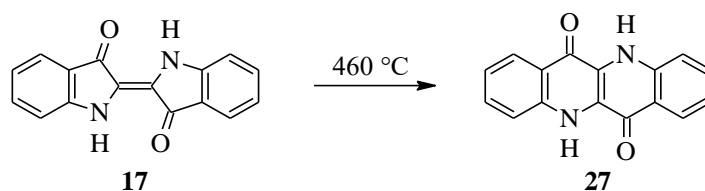
*Scheme 6: Heumann's (A)*⁵⁵ and *Pfleger's (B)*⁵⁶ synthetic pathways for the indigo molecule (**17**)

The isoindigo molecule (**18**) is another important member of the pigment group discussed in this chapter. The IID molecule is the congener of the ID molecule, and a general approach to the synthesis of IID derivatives is based on the acid catalysed condensation of isatin (**25**) with oxindole (**26**). The reaction is usually performed under reflux conditions and in the presence of a mixture of hydrochloric acid and acetic acid, as is shown in *Scheme 7*⁵⁷.



*Scheme 7: Condensation of isatin (25) with oxindole (26) to the resulting IID molecule 18*⁵⁷

The epindolidione molecule (EP, **27**) is the third and last important molecule discussed in this chapter. The EP molecule was first synthesized in 1934 by a relatively complicated multi-step reaction pathway⁵⁸. However, in 1995, Haucke and Graness⁵⁹ reported the preparation method of the EP molecule from the ID molecule by the thermal-induced isomerisation and they explained the isomerisation mechanism. The reaction proceeds at temperature more than 450 °C and under vacuum in the vapour phase with surprisingly high yields about 80 % (*Scheme 8*)⁵⁹.



Scheme 8: Thermal induced isomerisation of the ID molecule (**17**) to the EP molecule (**27**)

3.2.4 Derivatives of naphthyridinedione (NTD)

The derivative referred to as naphthyridinedione (NTD, **28**) has the systematic name 1,5-dihydro-1,5-naphthyridine-2,6-dione (**Figure 8**). Its backbone consists of the fused-ring system called naphthyridine, which is being formed by the fusion of two pyridine rings through two adjacent carbon atoms, where each ring thus contains one nitrogen heteroatom. A total of six isomers of naphthyridine can be formed (**Figure 9**). The name is dated to 1893 and is derived from the 1,8-naphthyridine derivative, which is considered as the naphthalene analogue of pyridine⁶⁰.

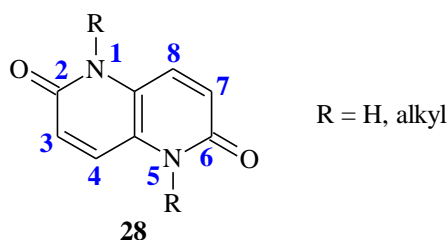


Figure 8: The general skeleton of the NTD molecule with atom numbering

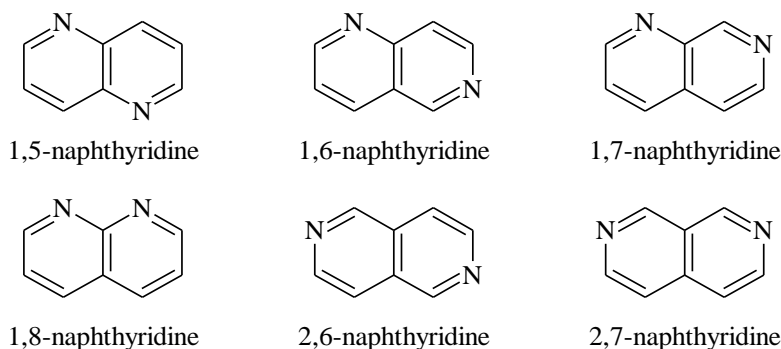
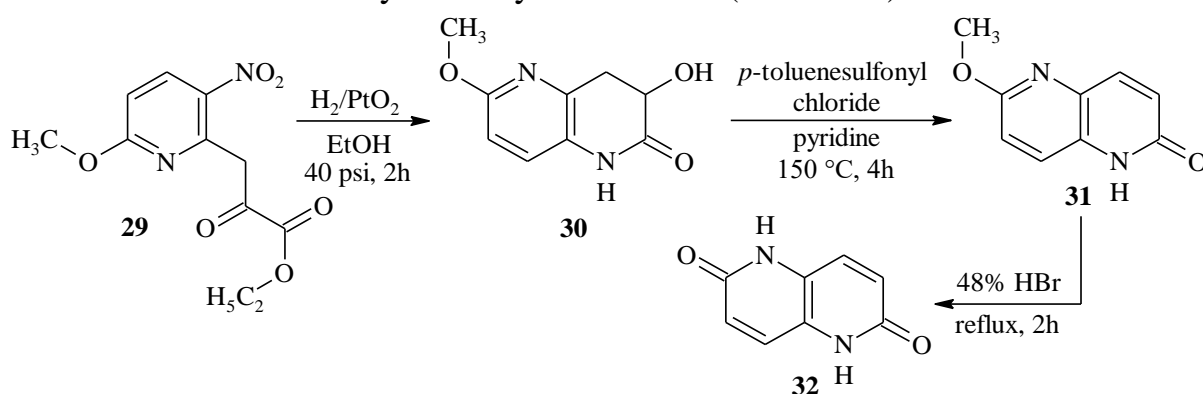


Figure 9: All possible isomers of the naphthyridine derivative

The NTD molecule was first synthesized in 1971 by Rapoport et al.⁶¹, and for more than four decades, there has been no mention of the application in organic electronics of this derivative. However, the turning point came in 2013, when the NTD molecule was a key fragment of the patent related to novel polymers containing one or more units derived from the NTD and their applications as organic semiconductors especially in the areas of OPV devices and organic photodetectors (OPD)⁶². In terms of structure, the NTD is the bis-lactam unit with an electron-deficient character, thus very similar to the DPP molecule, including its potential in

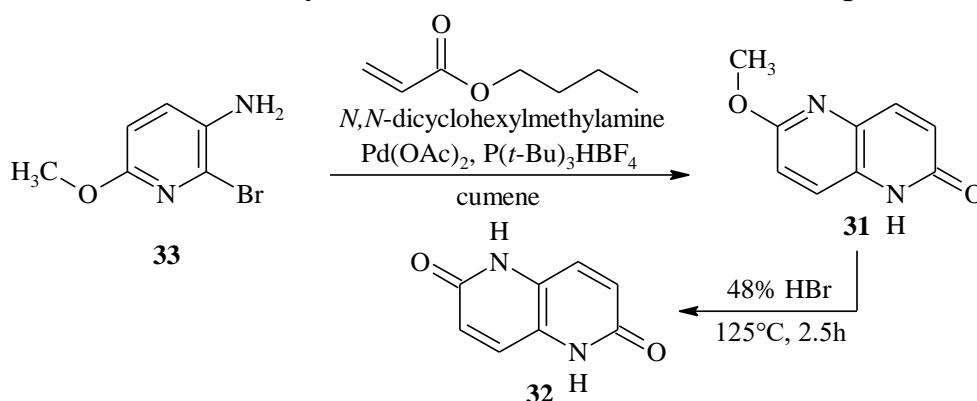
organic electronics applications. Although especially the difference in the ring sizes of DPP's and NTD's lactam units results in different electronic and photophysical properties, the NTD derivative again proved to be a very useful building block for organic electronics materials in 2016, when Park et al.⁶³ described a novel NTD based donor-acceptor type conjugated polymer.

The synthetic pathway for the preparation of the 1,5-dihydro-1,5-naphthyridine-2,6-dione molecule (**32**) first described in 1971 by Rapoport et al.⁶¹ started from ethyl 6-methoxy-3-nitro-2-pyridinepyruvate (**29**), which was subjected to reductive cyclization using platinum oxide. Thus, a new six-membered ring of 1,3,4-trihydro-3-hydroxy-6-methoxy-1,5-naphthyridin-2-one (**30**) is formed and then readily dehydrated by treatment with *p*-toluenesulfonyl chloride to the derivative **31**. Its subsequent transformation to the resulting NTD molecule (**32**) is performed by 48% hydrobromic acid with a very decent yield of 83 % (**Scheme 9**)⁶¹.



Scheme 9: The original synthetic pathway of the NTD molecule preparation described in 1971⁶¹

A novel and rather simpler synthetic pathway for the preparation of the NTD molecule was published in 2016 by Park et al.⁶³ (**Scheme 10**), when the derivative **31** is synthesized using an optimized *Heck* reaction from 2-bromo-6-methoxypyridin-3-amine (**33**)⁶⁴. The final NTD molecule is prepared by treatment of the formed molecule **31** with hydrobromic acid, the same as in the previous case.



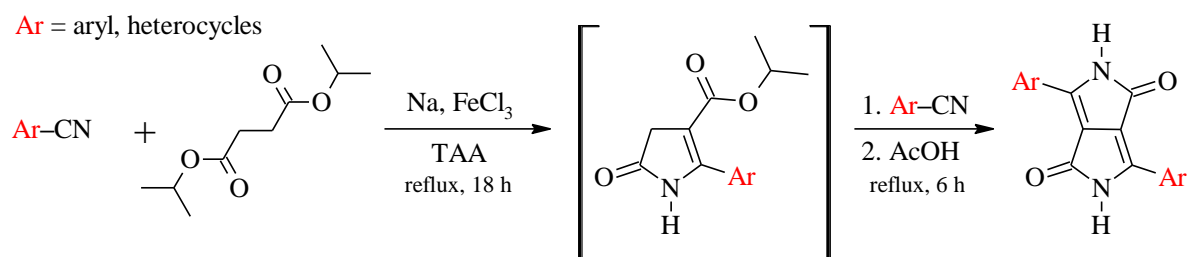
Scheme 10: Novel and simpler synthetic pathway of the NTD molecule preparation from 2016⁶³

4 EXPERIMENTAL PART

4.1 DPP DERIVATIVES

4.1.1 Synthesis of basic DPPs and with extended π -conjugation

A well-known and studied *succinic method* was used to prepare the target DPP derivatives. As depicted in **Scheme 11**, this method uses base-promoted condensation of aryl nitrile-derivative with succinic acid ester in an equimolar ratio of 2 to 1.



Scheme 11: General synthetic approach (“succinic method”) to preparation the DPP molecule

Diisopropyl succinate was specifically used as a starting material as an ester of succinic acid with branched alcohols, which are generally much less prone to the dimerization reaction by the *Claisen condensation* mechanism, leading to the formation of cyclic diester. Sodium *tert*-amyl alkoxide was used as the base due to its sufficient basicity to deprotonate succinic acid esters and, conversely, due to its relatively low nucleophilicity to the undesired nucleophilic addition to the cyano group of aryl nitriles. An in-depth, long-term study and optimization of this reaction has shown that performing in the presence of tertiary alkoxides as bases has a positive effect on the yield of the reaction^{42,43,65}.

Furthermore, it is well known that the character of an aromatic nitrile-derivative plays a crucial role in the formation of the DPP molecule. In general, electron-poor and sterically unhindered aromatic nitriles provide the highest yields, while on the other hand electron-rich and bulky nitriles exhibit much lower reactivity leading to significantly worse yields of the resulting DPPs⁴².

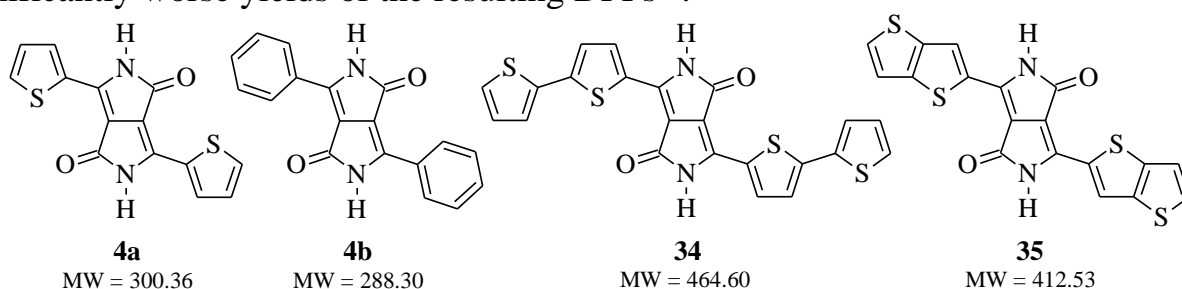


Figure 10: All four prepared basic N,N' -unsubstituted DPP derivatives

In this work, a total of four basic N,N' -unsubstituted DPP derivatives were prepared (**Figure 10**), and the obtained yields are in good agreement with the above regularities. While thiophene-2-carbonitrile as a small five-membered ring gave the DPP molecule in the highest yield obtained (**4a**, yield 59 %), the bulkier and

relatively electron-rich 2,2'-bithiophene-5-carbonitrile resulted in the DPP molecule in the lowest yield obtained (**34**, yield 35 %) when carrying out the reactions under the same conditions.

Table 1: Summary of yields of preparation of basic DPP derivatives

| DPP | 4a | 4b | 34 | 35 |
|-----------|----|----|----|----|
| Yield [%] | 59 | 52 | 35 | 41 |

In summary, all of the above-mentioned basic DPPs were prepared in moderate yields (**Table 1**) and then successfully used for further synthetic steps. The above synthetic procedure is very advantageous, both for laboratory and industrial scale^{36,66}. Its main benefits are simplicity, easy availability and low cost of starting materials, together with a relatively wide range of usable aromatic nitrile-derivatives. Purification of the obtained DPPs, which were suspended in refluxing methanol and filtered off while hot, was also very easily feasible, thus obtaining the materials in sufficient purity for further synthesis.

4.1.2 Synthesis of basic DPPs with alkylated side 3,6-aryl units

The basic *N,N'*-unsubstituted DPP derivatives form intermolecular hydrogen bonds ($-\text{NH}-\text{O}=\text{}$, **Figure 11**), which together with $\pi-\pi$ molecular stacking are responsible for exceptional thermal stability, high crystal lattice energies and excellent photostability of these DPPs. In addition, Głowacki et al.⁶⁷ described that even these *N,N'*-free DPPs could function as organic semiconductors when, based on the calculated charge transfer integrals, the H-bonded contacts between adjacent molecules can also contribute to charge transport in the crystal.

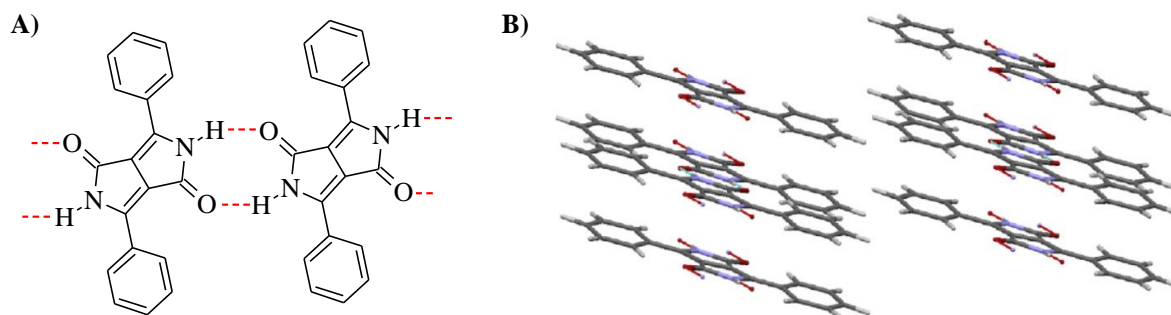


Figure 11: Molecular structure of the DPP with formed hydrogen bonds between adjacent molecules (A) and crystal structure of the DPP (B)⁶⁷, where the red lines indicate H-bonds.

On the contrary, the intermolecular H-bonds discussed above result in a very limited solubility of the resulting DPPs in most common organic solvents, which disables their solution processability and generally makes it very difficult to apply these derivatives in organic electronics. One of the solutions to increase their applicability is *N,N'*-alkylation, which, however, causes the interruption of hydrogen bonds and thus the resulting possible advantages mentioned above. Therefore, the aim was to prepare novel, as yet undescribed DPP derivatives, which will be *N,N'*-unsubstituted and, in addition, will contain alkyl chains on the 3,6-aromatic side

units, which could ensure a higher solubility of the resulting DPPs in common organic solvents and thus also their potential applicability. The structures of the three target such modified DPP derivatives are shown in the following **Figure 12**.

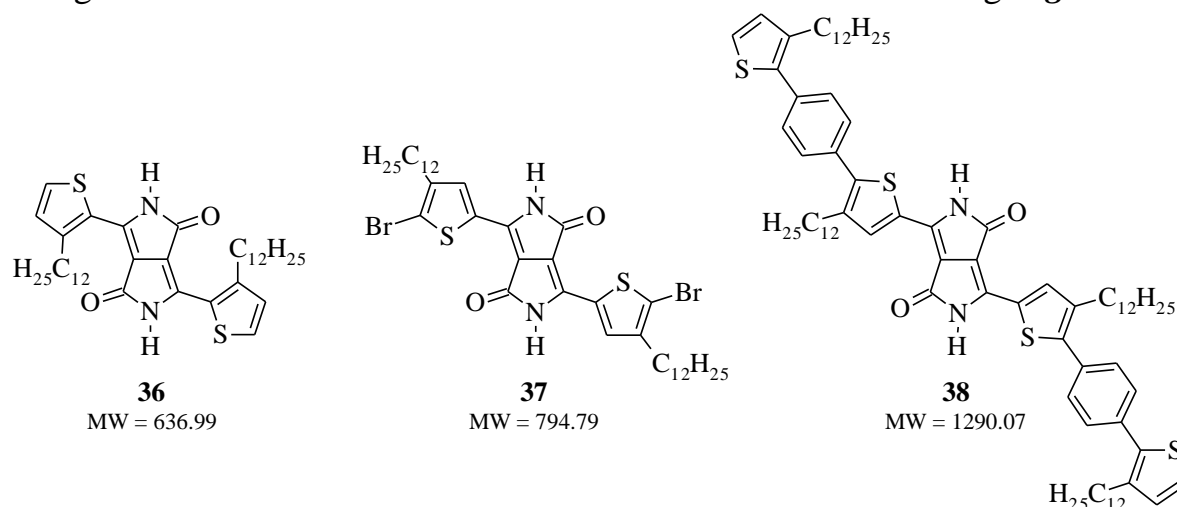


Figure 12: Three target basic DPP derivatives with alkylated side 3,6-aryl units

The *succinic method*, discussed in the previous chapter (4.1.1), was used to prepare the resulting three derivatives under the same conditions. Nevertheless, two of the three target derivatives were not successfully prepared, as shown in the following **Table 2**. In the case of the first-mentioned derivative **36**, the main reason for the failure of the reaction may be the steric hindrance of the starting aromatic nitrile caused by the dodecyl chains adjacent to the cyano groups. This their position and potential orientation into the DPP core could prevent the double-cyclization to the resulting DPP **36**, as this reaction is exceptionally susceptible to steric hindrance.

Table 2: Summary of yields of preparation of basic DPP derivatives with alkylated side 3,6-aryl units

| DPP | 36 | 37 | 38 |
|-----------|------------------|-----|------------------|
| Yield [%] | × / not prepared | 9.4 | × / not prepared |

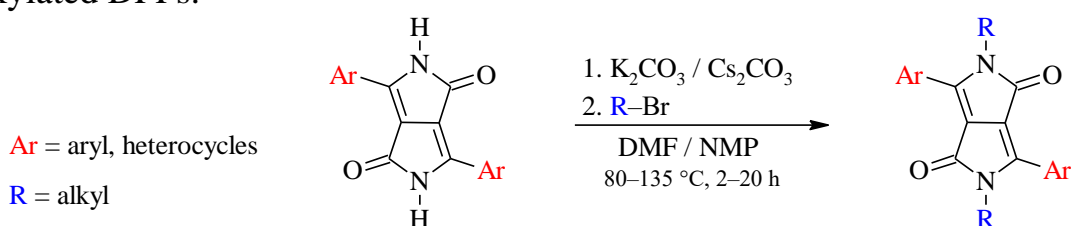
This assumption was confirmed by the successful preparation of DPP derivative **37**, where the starting nitrile contained dodecyl chains in position 4, which considerably reduced steric repulsions compared to the previous nitrile. Moreover, the orientation of the alkyl groups after successful cyclization to the DPP molecule was “out” from the DPP core, which could also facilitate the reaction progress. With respect that the resulting derivative **37** contained bromine atoms in its structure at the 5-positions of the thiophene side rings, it greatly expands its potential synthetic utilization to a diverse range of *cross-coupling* reactions.

The third and last target derivative **38** was not successfully prepared, as well as **36**. Due to the very low solubility of the “trimer-carbonitrile” in tertiary alcohol as the required solvent and thus the heterogeneous reaction features, the preparation of the derivative **38** by the *succinic method* was prevented.

4.1.3 Synthesis of *N*- and *O*-alkylated DPPs – approach A

N,N'-alkylation is one of the most significant and widely used modifications of DPPs. The reason for this modification, in addition to the well-known increase in solubility, was the incorporation of adamantyl substituents into the basic DPP derivatives discussed in *Chapter 4.1.1*. The new approach presented herein has been used for many other commercially obtained basic DPPs, which have been identified as high potential based on data from the literature, where they have shown interesting properties even with common alkyl substituents, such as 2-ethylhexyl. The contribution of these adamantyl substituents will then be studied on the resulting derivatives and compared with the already published exceptional results of ethyl-adamantyl thiophene DPP⁶⁸.

The reaction was performed by a well-described alkylation approach, where the basic DPP was first mixed with the appropriate base in a polar aprotic solvent (DMF) to form a DPP anion, followed by nucleophilic substitution with an alkylating agent to form an alkylated DPP product (*Scheme 12*)^{42,69}. DPP anion has an ambiguous character, which leads to competitive substitution on the nitrogen and oxygen atoms and thus also to a marked decrease in the formation of the *N,N'*-substituted product⁶⁹. The following *Table 3* provides an overview of all prepared *N,N'*-alkylated DPPs.



Scheme 12: General synthetic approach used for alkylation of DPPs

In most of the experiments performed, potassium carbonate was used as the base, DMF as the solvent, the reaction temperature was about 105 °C and the reaction time was several hours, as it has already been proved that these parameters do not have a very significant effect on the alkylation regioselectivity⁷⁰.

The finding that the character of alkyl chains has the most considerable influence on the course of alkylation of the DPP molecule is entirely in accordance with the literature data⁷¹. The relative reactivity of the used alkyl halides is shown in the following *Figure 13*. *N,N'*-alkylated products were most efficiently formed with linear dodecyl bromides, with a significant decrease in yields being observed for branched 2-ethylhexyl bromides. A similar or slightly worse *N,N'*-alkylation progress was observed with bulky 1-(2-bromoethyl)adamantane. As expected, the very worst course of the reaction was obtained using 1-(bromomethyl)adamantane having a neopentyl character, which is an undesirable structure for nucleophilic substitution.

Table 3: Summary of all prepared *N,N'*-alkylated DPPs by the alkylation approach

| <i>N,N'</i> -alkylated DPP derivative | | | Yield [%] |
|---------------------------------------|---------------------------------|------------------------------------|-----------------|
| DPP | Ar | R | |
| 39 | 2-thienyl | dodecyl | 75 |
| 40a | 2-thienyl | 2-ethylhexyl | 41 |
| 41a | 2-thienyl | ethyladamantyl | 36 |
| 42 | 2-thienyl | methyladamantyl | 7 |
| 43 | benzofuranyl-2-thienyl | dodecyl | 6 |
| 44 | benzofuranyl-2-thienyl | ethyladamantyl | 3 ^a |
| 45 | 2-thieno[3,2- <i>b</i>]thienyl | ethyladamantyl | 7 ^a |
| 46 | 2-bithienyl | 2-ethylhexyl | 16 ^b |
| 47 | 2-bithienyl | methyladamantyl | — |
| 48 | 2-bithienyl | ethyladamantyl | 14 ^b |
| 49 | phenyl | dodecyl | 63 |
| 50 | phenyl | 2-ethylhexyl | 12 |
| 51 | phenyl | ethyladamantyl | 14 |
| 52 | <i>p</i> -cyanophenyl | ethyl 2-(<i>N,N'</i> -DPP)acetate | 13 |
| 53 | 2-naphthyl | ethyladamantyl | 5 ^b |

^a based on NMR analysis, the obtained material was contaminated with *N,O'*-alkylated product

^b the highest yield obtained from the experiments reported herein (leading to the optimization)



Figure 13: Relative reactivity of alkyl halides used for alkylation of DPPs

In addition, it also turned out that the side 3,6-aromatic substituents in the DPP molecule had a significant effect on the course of *N,N'*-alkylation. From the obtained experimental data (**Table 3**), the range of these substituents was assembled according to the decreasing yield of *N,N'*-alkylation and is shown in the following **Figure 14**. It is obvious that with the increasing bulkiness of these substituents, the yield of the reaction decreases substantially. Thus, for example, when comparing the incorporation of ethyladamantyl substituents, by far the highest yield of *N,N'*-

alkylated product was obtained with the simplest thienyl-DPP (36 %), while a large decrease in yield (14 %) was observed for bithienyl-DPP. In the case of the most complex and bulky benzofuranyl-thienyl-DPP, it was difficult to isolate the *N,N'*-alkylated product in sufficient purity at all (<3%).

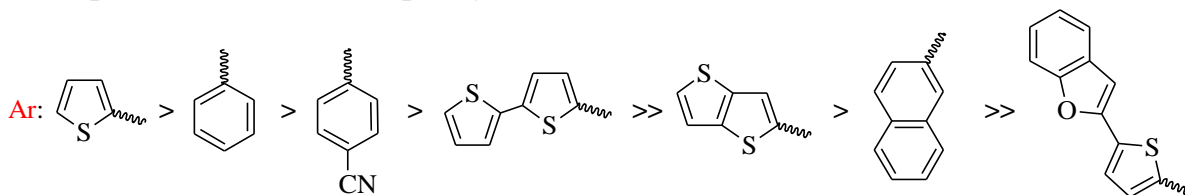


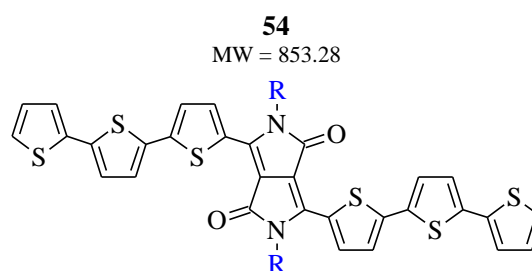
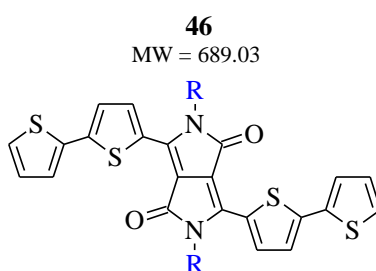
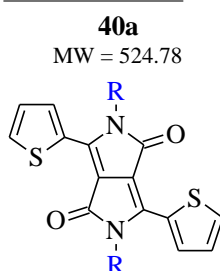
Figure 14: Relative reactivity of DPPs used depending on their 3,6-aromatic substituents

Based on the findings obtained from the performed experiments, it can be concluded that the temperature and time of the reaction have an important effect on the yield of *N,N'*-alkylation, but in a relatively small range. Rather, the suitable setting of these parameters can prevent especially the undesired course of the reaction leading to decomposition products. On the other hand, the nature of the substituents (both the side 3,6-aromatics and alkyl chains used for the reaction), especially in terms of their bulkiness, have a crucial influence on the reaction yield.

4.1.4 Synthesis of *N*- and *O*-alkylated DPPs – approach B

Another synthetic goal was to prepare six DPP derivatives **40a**, **41a**, **46**, **48**, **54** and **55** (**Figure 15**) in sufficient quantities (>50 mg) and purity for a comprehensive study of optical and electrical properties. It was focused on the effect of the alkyl chains character (branched vs bulky) together with the prolongation of the π -conjugation on these properties.

R = 2-ethylhexyl:



R = ethyladamantyl:

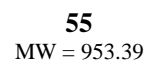
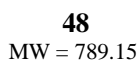
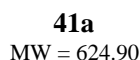
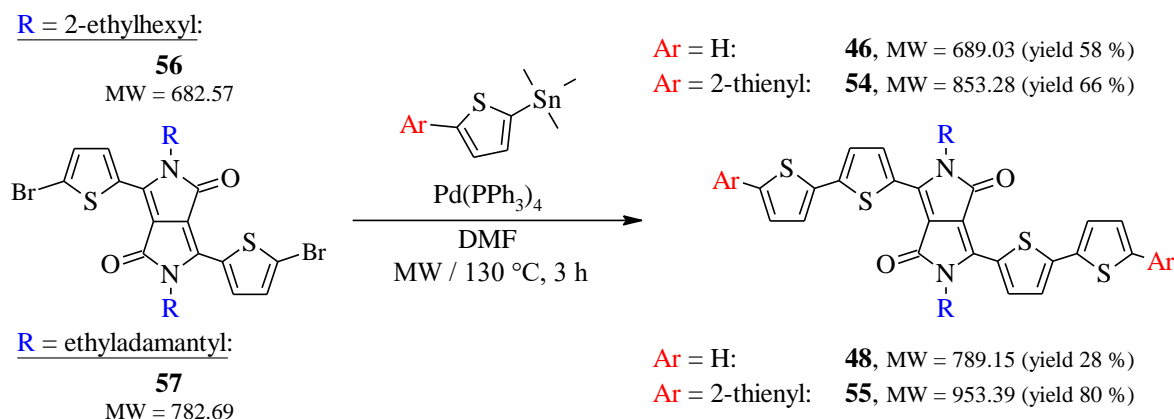


Figure 15: Six target DPP derivatives with different alkyl chains and prolonged π -conjugation

Derivatives **40a** and **41a** were easily prepared by the above-discussed alkylation method. In contrast, derivatives **46** and **48** were relatively complicated to obtain by *N,N'*-alkylation in the required amount, and especially derivatives **54** and **55** could not be prepared at all by this method due to the failure of the basic *N,N'*-unsubstituted terthiophene-DPP preparation, as already mentioned. Thus, an

alternative synthetic path based on the *Stille cross-coupling* reaction was used for the last four derivatives. (*Scheme 13*)⁷².



Scheme 13: General synthetic approach using *Stille cross-coupling* reaction for the preparation of *N,N'*-alkylated DPPs with prolonged π -conjugation

Table 4: Summary of four prepared *N,N'*-alkylated DPPs by the *Stille cross-coupling* approach

| DPP | 46 | 48 | 54 | 55 |
|-----------|-------------------|------|------|-------------------|
| Yield [%] | 57.6 ^a | 28.3 | 65.8 | 79.5 ^a |

^a the highest yield obtained from the experiments reported herein (leading to the optimization)

The synthesis of the four mentioned derivatives was carried out under microwave-assisted synthesis, in which the reaction mixture was fast heated to 90 °C in a microwave reactor and after 10 min, the mixture was cooled rapidly to 60 °C (repeated 4×). The mixture was then heated to 115 °C (130 °C, respectively) and maintained at this temperature for 2.5 h (2 h, respectively). Subsequently, the reaction was quenched and worked up to isolate the desired products.

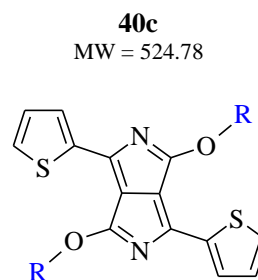
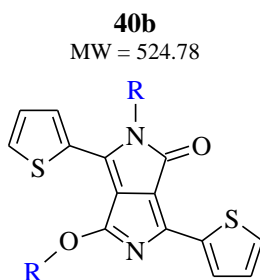
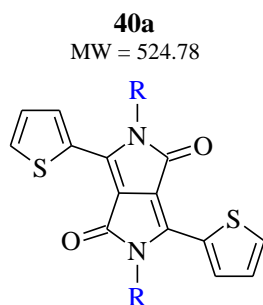
In all cases, Pd(PPh₃)₄ was used as a catalyst for the *Stille cross-coupling* reaction in DMF. Bithienyl-DPP derivatives **46** and **48** were initially prepared only in yields ranging from 28–29 % using a maximum temperature of 115 °C for 2.5 h. Increasing the temperature to 130 °C and shortening the reaction time to 2 h provided more than double the yield (57.6 %) in the case of derivative **46**. The same trend was observed in the preparation of derivative **55** when a much higher yield was achieved from the previous 63.5 % to almost 80 %. The synthetic procedures of derivatives **48** and **54** were not optimized, as they were already obtained in the moderate yields.

4.1.5 Comprehensive study of selected series of DPPs⁷³

Two series of thienyl-DPP derivatives alkylated with 2-ethylhexyl and ethyladamantyl chains were selected (*Figure 16*). The main goal was to isolate all forming *N,N'*-, *N,O'*- and *O,O'*-substituted products and subsequently subject them to an in-depth study of thermal and optical properties, both in solution and in thin layers. This comprehensive study was focused mainly on the study of the effect of

the alkyl chains' character and their binding position in the DPP molecule on physicochemical properties of the resulting derivatives.

R = 2-ethylhexyl:



R = ethyladamantyl:

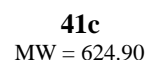
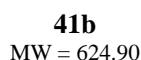
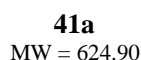


Figure 16: Summary of the prepared and isolated two series of alkylated DPP derivatives

Table 5: Summary of yields from preparation of *N,N'*-, *N,O'*- and *O,O'*-alkylated DPPs

| DPP | <i>N,N'</i> - | <i>N,O'</i> - | <i>O,O'</i> - |
|----------------|---------------|---------------|---------------|
| 2-Ethylhexyl | 40a | 40b | 40c |
| Yield [g/%] | 41 | 18 | 3 |
| Ethyladamantyl | 41a | 41b | 41c |
| Yield [g/%] | 36 | 20 | 6 |

As can be seen from **Table 5** summarizing the yields for the preparation of the target DPP derivatives, the reactivity of both alkylating reagents was similar, as already discussed (**Figure 13**). Due to the bulkiness of the adamantyl chains and thus the increase in possible steric repulsions, a slight decrease in yield was observed for the resulting *N,N'*-substituted derivative, while the yield of *O*-substitution slightly increased. In particular, the yield of the symmetrical *O,O'*-product was doubled compared to the branched 2-ethylhexyl substituent.

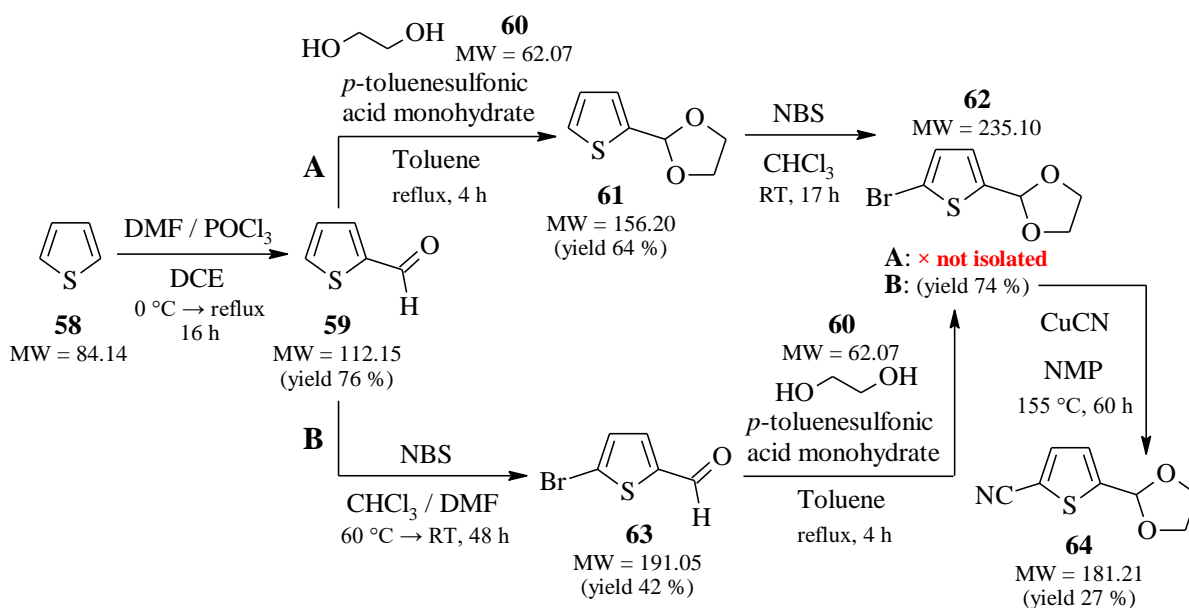
In summary, it has been found that *O*-substitution generally leads to a significantly worse thermal stability of the resulting materials and a reduction in the formation of crystalline structures compared to *N*-alkylation. However, the 2-ethylhexyl side chains promote the formation of thin layer crystal structures based on the asymmetrically *N,O'*-substituted derivative, while the ethyladamantyl chains show a better molecular arrangement in the case of symmetrical *O,O'*-derivative according to the obtained optical and thermal data. Moreover, the ethyladamantyl substituent contributes to a significant increase in the melting points of all studied regioisomers and also improves their thermal stability compared to 2-ethylhexyl. In general, both the type of alkyl chain used and the position of its attachment in the DPP molecule have a major effect on the properties of the thin films. All these findings were successfully published in an impacted journal⁷³.

4.1.6 Incorporation of electron-accepting groups into DPPs

Based on the information discussed in the review part of the doctoral thesis, the incorporation of dicyanovinyl groups into the DPP skeleton brought in many cases very interesting electrical properties of the resulting derivatives^{74,75}. Therefore, the aim here was to modify the exceptional ethyladamantyl-thienyl-DPP derivative (**41a**) with these functional groups.

Due to the extremely limited solubility of the starting *N,N'*-ethyladamantyl DPP derivative (**41a**), it was not possible to prepare its diformyl derivative by lithiation and subsequent formylation using DMF/*N*-formylpiperidine, unlike the 2-ethylhexyl analogue. Therefore, an alternative synthetic path was chosen, involving the incorporation of formyl functional groups already into the DPP skeleton in the form of acetal-protected groups.

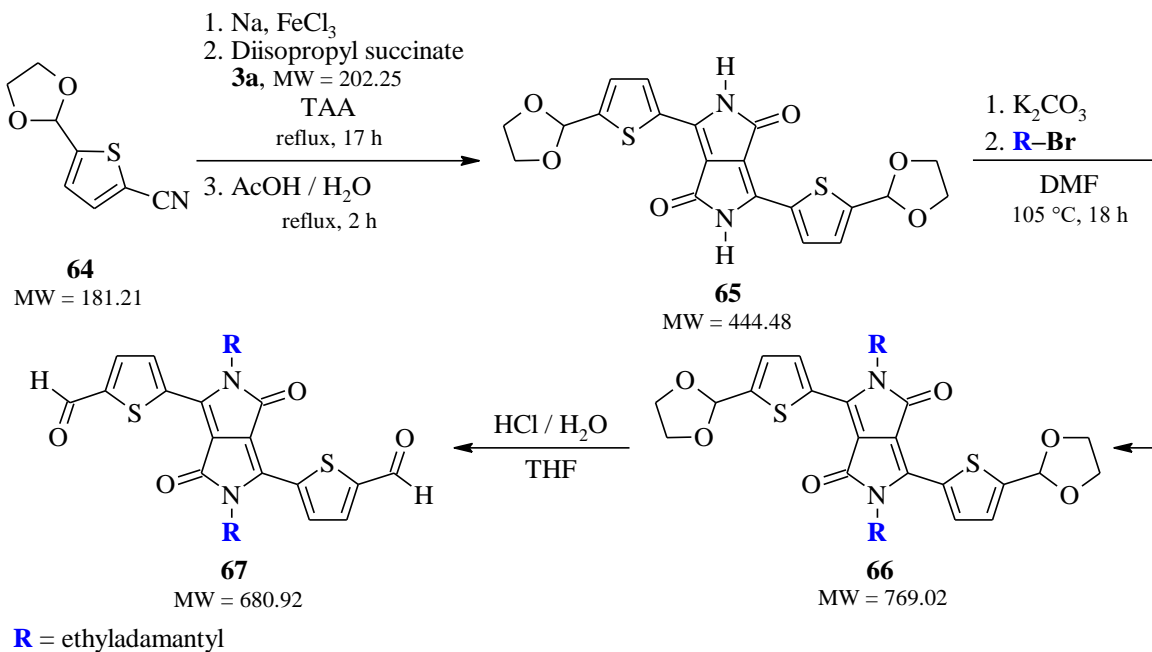
Thiophene-carbonitrile **64** was synthesized *via* a two-step synthesis started with thiophene (**58**), which was subjected to a classical *Vilsmeier-Haack* reaction to form product **59** in a yield of 76 %, followed by protection of the formyl group to give derivative **61**. Intermediate **61** was subsequently brominated to afford **62** (**approach A**, *Scheme 14*). However, bromination of derivative **61** exhibited poor regioselectivity according to GC-MS analysis, and therefore pure product **62** was not isolated, and an alternative synthetic approach had to be applied (**approach B**, *Scheme 14*).



Scheme 14: Synthetic approaches A/B used to prepare targeted aromatic nitrile 64

In the second synthetic path, derivative **59** was first selectively brominated to give pure product **63** with a purity of 98 % (GC-MS) in a yield of 42 %. The obtained derivative **63** was then subjected to formyl group protection to successfully afford the product **62** in an excellent yield of 74 %. In the last step, the nucleophilic substitution of the bromine atom for a cyano group was performed according to a known procedure⁷⁶; thus obtaining the desired aryl nitrile **64** in a yield of 27 %.

The following **Scheme 15** outlines the ongoing synthetic procedure to obtain the desired diformyl derivative from *N,N'*-ethyladamantyl-thienyl-DPP (**41a**). The preparation of the basic DPP (**65**) will be realized by the classical *succinic method*⁴³. Subsequently, a conventional base catalysed alkylation^{42,69} will be performed focusing on the isolation of the *N,N'*-alkylated product (**66**). In the last step, the acid-catalysed deprotection of derivative **66** using dilute hydrochloric acid solution⁷⁷ will be carried out to give the final diformyl derivative **67** as starting material for the already verified *Knoevenagel condensation* with malononitrile to afford the desired dicyanovinyl DPP derivative.

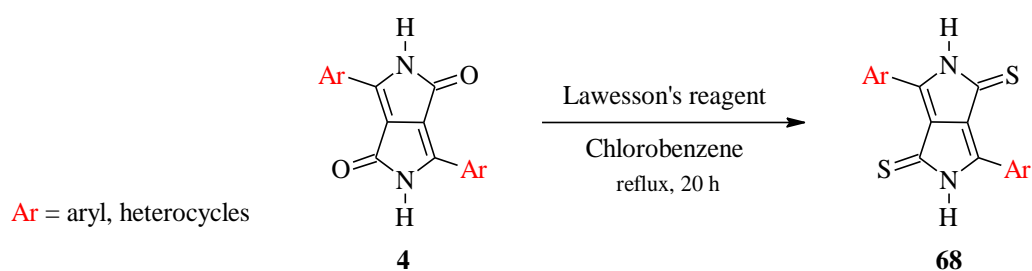


Scheme 15: The proposed synthetic approach for the preparation of diformyl-DPP derivative **67**

This synthetic path (**Scheme 15**) has not yet been realized due to time constraints. In principle, however, there should be nothing to prevent the successful preparation of the targeted derivative.

4.1.7 Synthesis of thioketo analogues of DPPs (DTPPs)

The transformation of basic DPP derivatives into their thioketo analogues was performed *via* the well-described thionation^{78,79} using Lawesson's reagent in chlorobenzene (**Scheme 16**). The reaction mixtures were stirred for 20 h at reflux, and the desired products were isolated in yields from 52 % to 96 % (**Table 6**), which is in accordance with the literature^{78,79,80}.



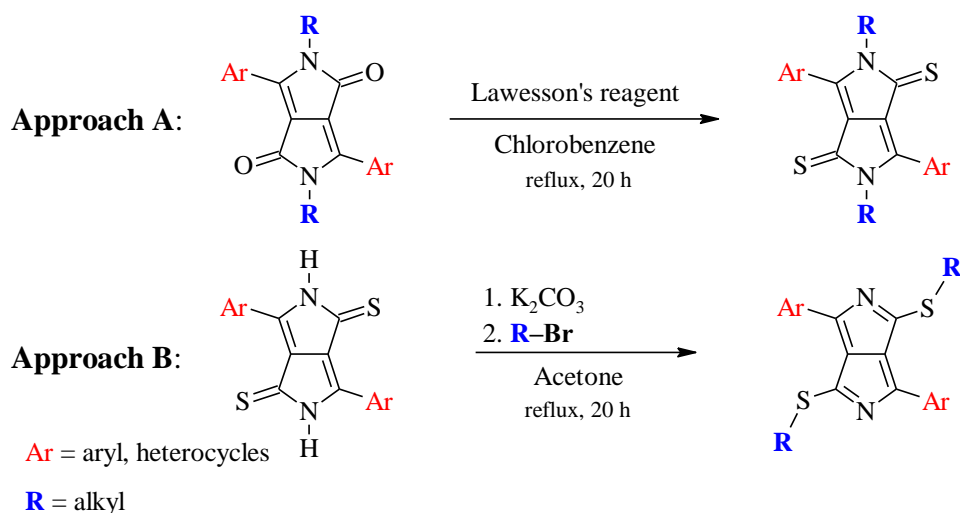
Scheme 16: General synthetic approach used for thionation of DPPs using Lawesson's reagent

Table 6: Summary of all prepared dithioketopyrrolopyrroles (DTPPs)

| DPP | 68a | 69 | 68b | 70 | 71 |
|-----------|-----------|-------------|--------|------------|-------------|
| Ar | 2-thienyl | 2-bithienyl | phenyl | 2-naphthyl | 4-pyridinyl |
| Yield [%] | 87 | 96 | 82 | 87 | 52 |

The prepared derivatives were used both for next synthetic steps (discussed further) and for an in-depth study of their physicochemical properties, which are currently the subject of intensive research.

Furthermore, the series of *N*- and *S*-alkylated DTTP derivatives were prepared. In terms of reactivity and reaction mechanism, it is necessary to use different synthetic approaches for the preparation of these two series of alkylated products (**Scheme 17**).



Scheme 17: Two synthetic approaches used to prepare *N*- (**A**) and *S*-alkylated (**B**) DTTPs

For the selective preparation of *N,N'*-alkylated DTTPs, it is necessary to start with already *N,N'*-alkylated DPP derivatives and subject them to thionation using Lawesson's reagent (**Approach A**, **Scheme 17**). The reason is the relative reactivity of DPP- vs DTTP-anion to nucleophilic substitution, where the sulphur-anion is a better nucleophile than the nitrogen-anion. Therefore, alkylation occurs primarily at *S*-positions in the case of the DTTP molecule, which thereby largely gives the second desired product: *S,S'*-alkylated DTTPs (**Approach B**, **Scheme 17**). Based on

the experiments performed, it is impossible to isolate any proportion of *N,N'*-alkylated DTPPs using synthetic **approach B**.

Table 7: Summary of all prepared *N*- and *S*-alkylated DTPP derivatives

| DPP | Approach | Ar | R | Yield [%] |
|-----------|----------|-------------|-----------------|----------------|
| 72 | A | 2-thienyl | ethyladamantyl | 79 |
| 73 | A | phenyl | ethyladamantyl | 61 |
| 74 | B | 2-thienyl | dodecyl | 47 |
| 75 | B | 2-thienyl | ethyladamantyl | 63 |
| 76 | B | 2-thienyl | methyladamantyl | — ^a |
| 77 | B | 2-bithienyl | ethyladamantyl | 20 |
| 78 | B | phenyl | dodecyl | — ^a |
| 79 | B | phenyl | ethyladamantyl | 30 |

^a product was most likely completely decomposed

Two derivatives substituted with ethyladamantyl chains (**72** and **73**) were successfully prepared by synthetic **approach A** in yields exceeding 60 %. Furthermore, a total of four derivatives were successfully prepared by synthetic **approach B** (**Table 7**). The reactions proceeded analogously to the alkylation of the basic DPP derivatives described-above, i.e. the base-promoted nucleophilic substitution of alkyl bromides. In all cases, poor product stability was observed; however, the effect of degradation due to light exposure is known from the literature⁸¹ for alkylated DTPP analogues. Nevertheless, all manipulation were performed under ambient conditions with access to light, which probably led to the complete decomposition of derivatives **76** and **78**. The properties of isolated products are further the subject of an in-depth study of physicochemical properties.

4.2 BDF DERIVATIVES

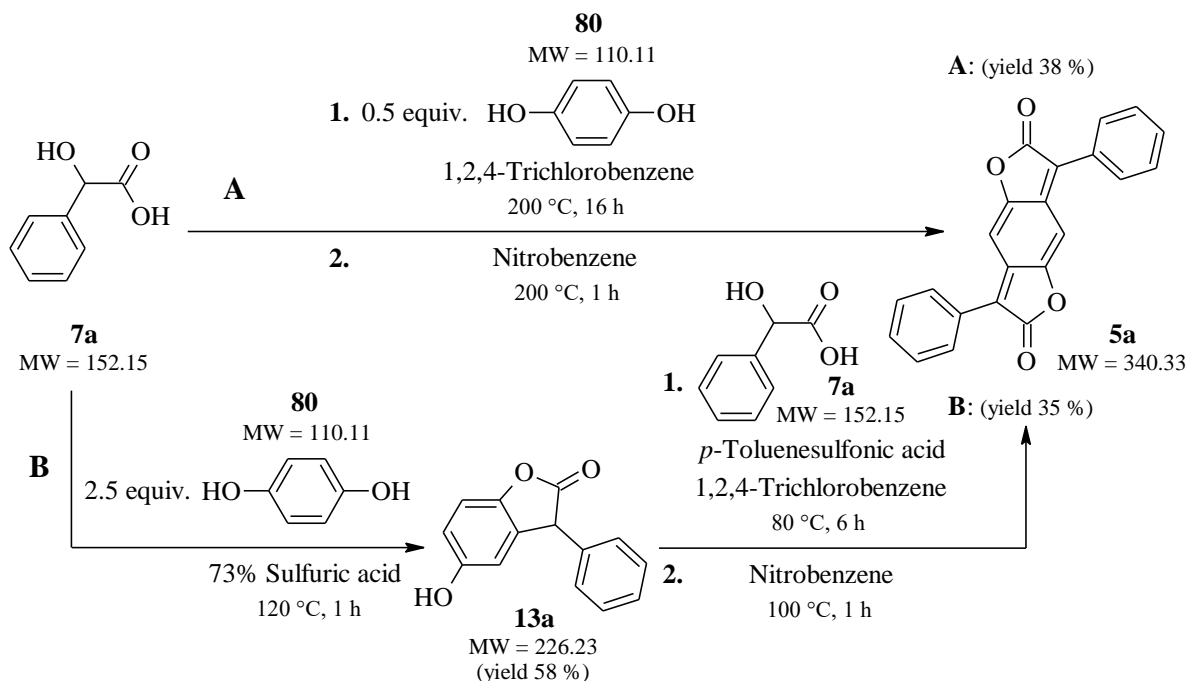
4.2.1 Symmetrical BDF derivatives

The mechanism of the BDF skeleton formation was described in detail in the review section (3.2.2). The key starting materials are α -hydroxy acids (AHAs), which react with hydroquinone in acidic conditions, and the resulting BDF molecule is formed after double cyclization followed by oxidation of the di-condensate formed (**Scheme 2–Scheme 4**)^{48,49,50}.

In the beginning, the main interest was focused on the verification of the synthetic possibilities for the preparation of the basic diphenyl-BDF derivative, already described in the literature^{46,47} (**Scheme 18**).

Two synthetic approaches were used: **Approach A** uses the reaction of mandelic acid (**7a**) with 0.5 equimolar amount of hydroquinone (**80**) leading directly to double

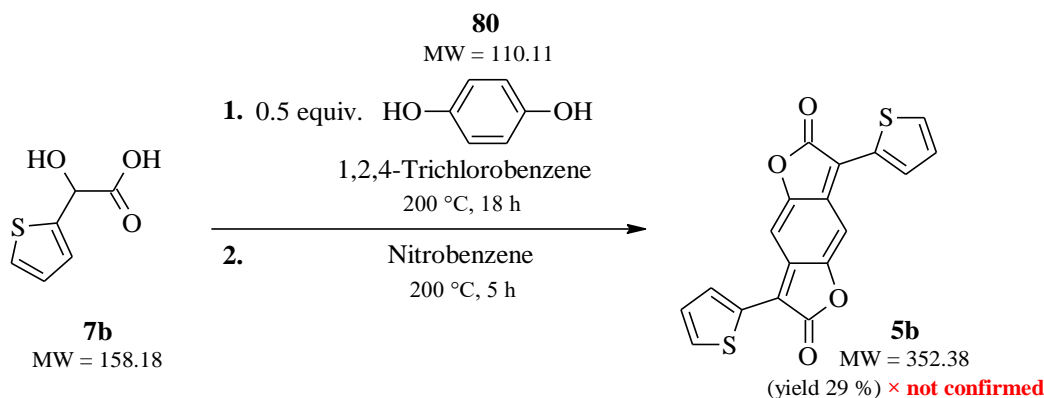
cyclization. After oxidation with nitrobenzene, the desired BDF derivative was prepared in a yield of 38 % (lit. 35 %⁴⁶). **Approach B** first involves the reaction of mandelic acid (**7a**) with an excess (2.5 equiv.) of hydroquinone (**80**) to prepare the mono-condensate **13a**⁵⁰, which was isolated in 58% yield, followed by reaction with mandelic acid (**7a**) in a stoichiometric ratio of 1:1 to give the di-condensate. After its oxidation, the resulting BDF derivative was prepared in a yield of 35 %.



Scheme 18: Two synthetic approaches (A/B) used to prepare the diphenyl-BDF derivative **5a**

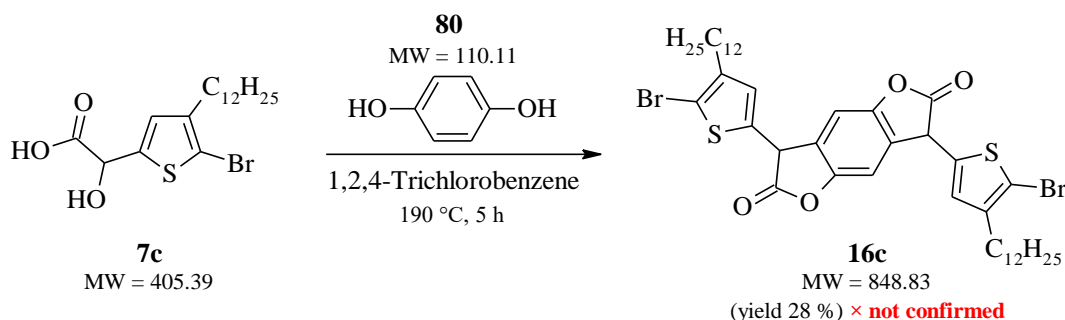
According to the experimental results, both of the above-mentioned synthetic paths are applicable. **Approach A** provided higher overall yields, on the other hand **approach B** opens the possibility of preparing asymmetric BDF derivatives, which will be discussed further.

However, the main goal was to prepare a thiophene analogue of the BDF derivative and thus key thiophene-based AHAs were synthesized (**7b** and **7c**). The prepared derivative **7b** was subsequently used for an analogous synthesis of the BDF derivative, as in the case of **approach A** in the previous case (**Scheme 18**). The reaction time of the condensation and the following oxidation were extended, and probably the desired product **5b** was obtained in a yield of 29 % as a dark black-blue solid (**Scheme 19**). Nevertheless, the structure of the obtained material could not be confirmed, probably due to its extremely limited solubility in most organic solvents. This significantly hampered the possibilities of both its analysis and purification only for stirring in refluxing toluene followed by the filtration while hot. Structural analysis was performed using ¹H NMR spectroscopy measured in hot DMSO-d₆; however, the spectra obtained were very indeterminate, and it was not possible to confirm the structure of product **5b**.



Scheme 19: Preparation of a novel dithienyl-BDF derivative **5b**

Therefore, the prepared derivative containing side solubilising alkyl groups **7c** was used for the direct synthesis of the di-condensate by its reaction with 0.5 equiv. of hydroquinone (**80**), using the same synthetic method mentioned above (**Scheme 20**). However, the oxidation was not performed immediately, but the product **16c** was isolated in 28% yield as a dark blue-black solid and purified by crystallisation from 1:1 toluene/methanol. ¹H NMR analysis again did not confirm the structure of the desired product **16c**, and therefore its successful preparation could not be verified.



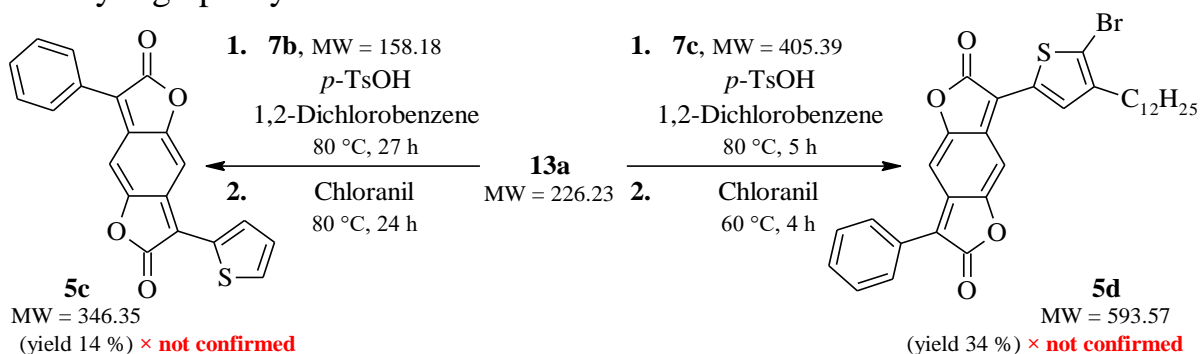
Scheme 20: Preparation of 3,7-bis(5-bromo-4-dodecyl-2-thienyl)-3,7-dihydro-BDF (**16c**)

4.2.2 Asymmetrical BDF derivatives

The obtained and structurally confirmed intermediates from the previous synthetic paths were used for preparation two asymmetric derivatives BDF, **5c** and **5d** (**Scheme 21**). Both reactions started with phenyl mono-condensate **75a** as starting material, and the reaction conditions were set according to the verified synthetic **approach B** in the synthesis of symmetric phenyl-BDF **5a** (**Scheme 18**), only the oxidising agent chloranil was used instead of nitrobenzene.

Thienyl-AHA **7b** was reacted with 1.0 equiv. of mono-condensate **13a** in the presence of *p*-toluenesulfonic acid and after subsequent oxidation with chloranil, probably product **5c** was obtained in a yield of 14 %. Under the same conditions, but with a shortened reaction time, **13a** reacted with β -alkylated-thienyl-based AHA **7c**, followed by oxidation with chloranil to give the potential product **5d** in a decent

yield of 34 %. Both materials obtained, **5c** and **5d**, had the character of dark violet-black high-melting solids (T_{MP} of **5c** was above 320 °C), exhibiting typical pigment properties, as expected. However, none of these derivatives could be obtained in sufficiently high purity to confirm their structure.

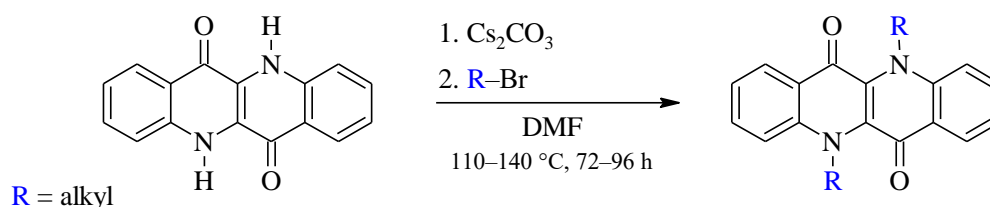


Scheme 21: Preparation of asymmetrical BDF derivatives **5c** and **5d**

So even here, the result from previous experiments in the preparation of BDF derivatives containing thiophene units was repeated. In all cases, the materials having organic pigment properties were isolated; however, their structure could not be confirmed by conventional characterization techniques as, e.g. NMR spectroscopy. Considerable efforts will undoubtedly be further made to prepare and validate the target thienyl-BDFs mentioned herein.

4.3 EP DERIVATIVES

4.3.1 Synthesis of N,N' -alkylated EPs



Scheme 22: General synthetic approach used for alkylation of EP molecule

The base catalysed nucleophilic substitution of alkyl bromides was used to prepare the two target N,N' -alkylated EP derivatives (**Scheme 22**), the same synthetic approach as for the DPP derivatives discussed above^{42,69}. The alkylating reagents used were 1-(bromomethyl)adamantane and 1-(2-bromoethyl)adamantane.

Both reactions required a high temperature above 100 °C and long reaction time in the order of several tens of hours. The yield in both syntheses was only percent units (**Table 8**), which was probably due to the bulkiness of the adamantyl substituents. As expected, the yield was worse in the case of substitution with methyladamantyl chains (**27b**) due to the more difficult steric accessibility of the neopentyl chain compared to ethyladamantyl, as already discussed for DPPs. The regioselectivity of the reactions was very poor according to TLC analysis and a

number of by-products, most likely *O*- and mono-substituted, were observed. These by-products were not isolated and identified in this work; however, they significantly devalued the yields of the desired molecules **27a** and **27b** (**Figure 17**).

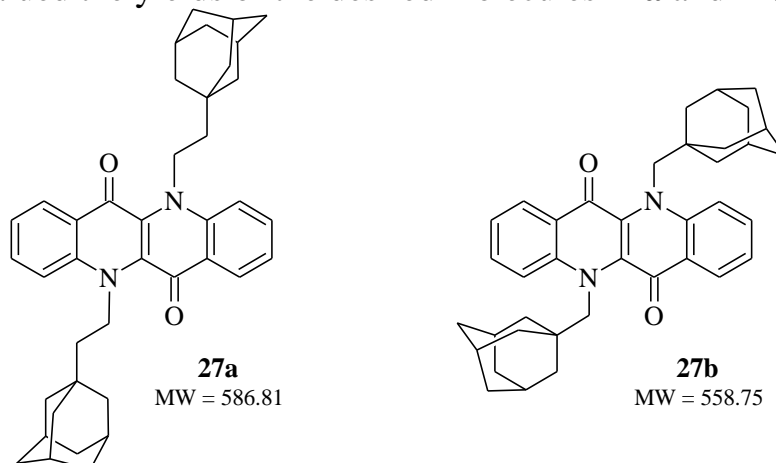


Figure 17: Structures of two prepared derivatives of EP – **27a** and **27b**

Table 8: Summary of the preparation of two EP derivatives – **17a** and **17b**

| EP | Temperature [°C] | Reaction time [h] | Yield [%] |
|------------|------------------|-------------------|-----------|
| 27a | 110 | 72 | 3.6 |
| 27b | 140 | 96 | 2.5 |

Further characterizations of thermal, optical and electrical properties will be provided and, in addition, the contribution of adamantyl substituents to the resulting properties of EP derivatives in comparison with DPPs will be investigated.

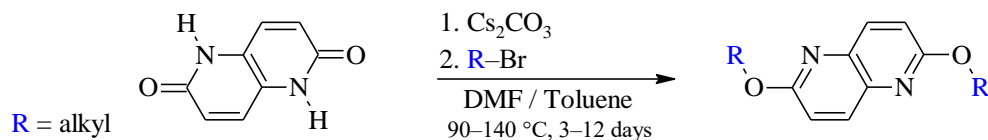
4.4 NTD DERIVATIVES

4.4.1 Synthesis of *O,O'*-alkylated NTD derivatives

Alkylation of the NTD molecule *via* nucleophilic substitution is one of the most significant and widely used modifications of these derivatives. Although the NTD molecule containing dilactam groups is structurally similar to DPP, the alkylation process is significantly different here caused by the position of the nitrogen heteroatoms in the molecule together with steric factors. Therefore, the asymmetric *N,O'*-derivative is always formed as a majority, while *N,N'*-alkylated is the least formed^{63,82}, which is the exact opposite of DPP alkylation^{42,69}. Since asymmetric *N,O'*-products were not evaluated as potentially interesting materials in terms of structural properties and ability to self-assembly in thin layers; the aim was to prepare and isolate symmetrical *O,O'*-alkylated products. The alkylation chains were used analogously to the modification of DPP derivatives: dodecyl as linear, 2-ethylhexyl as branched and ethyladamantyl as bulky.

The reaction was performed by the above-mentioned synthetic approach using a base (Cs_2CO_3) and an alkyl bromide (**Scheme 23**). Various solvents were tested to improve the regioselectivity of the alkylation (**Table 9**) but without significant

effect. The most important parameter appeared to be a longer reaction time of the order of several days. Ethyladamantyl bromide exhibited the best regioselectivity of the alkylation leading to the formation of the *O,O'*-substituted NTD derivative (**83**), which was prepared in the highest yield of about 70 % compared to other derivatives.



Scheme 23: General synthetic approach used for alkylation of NTD molecule

Table 9: Summary of the preparation of *O,O'*-alkylated NTD derivatives

| NTD | 81 | 82 | 83 | 83^a |
|-------------------|-------------|---------------|----------------|-----------------------|
| R | dodecyl | 2-ethylhexyl | ethyladamantyl | ethyladamantyl |
| Solvent | DMF | DMF | DMF / Toluene | DMSO |
| Temperature [°C] | 90 | 90 | 140 | 135 |
| Reaction time [h] | 96 (4 days) | 288 (12 days) | 72 (3 days) | 42 h |
| Yield [%] | 26 | 4.6 | 72 | 67 |

^a there has been an effort to obtain as much *N,N'*-product as possible

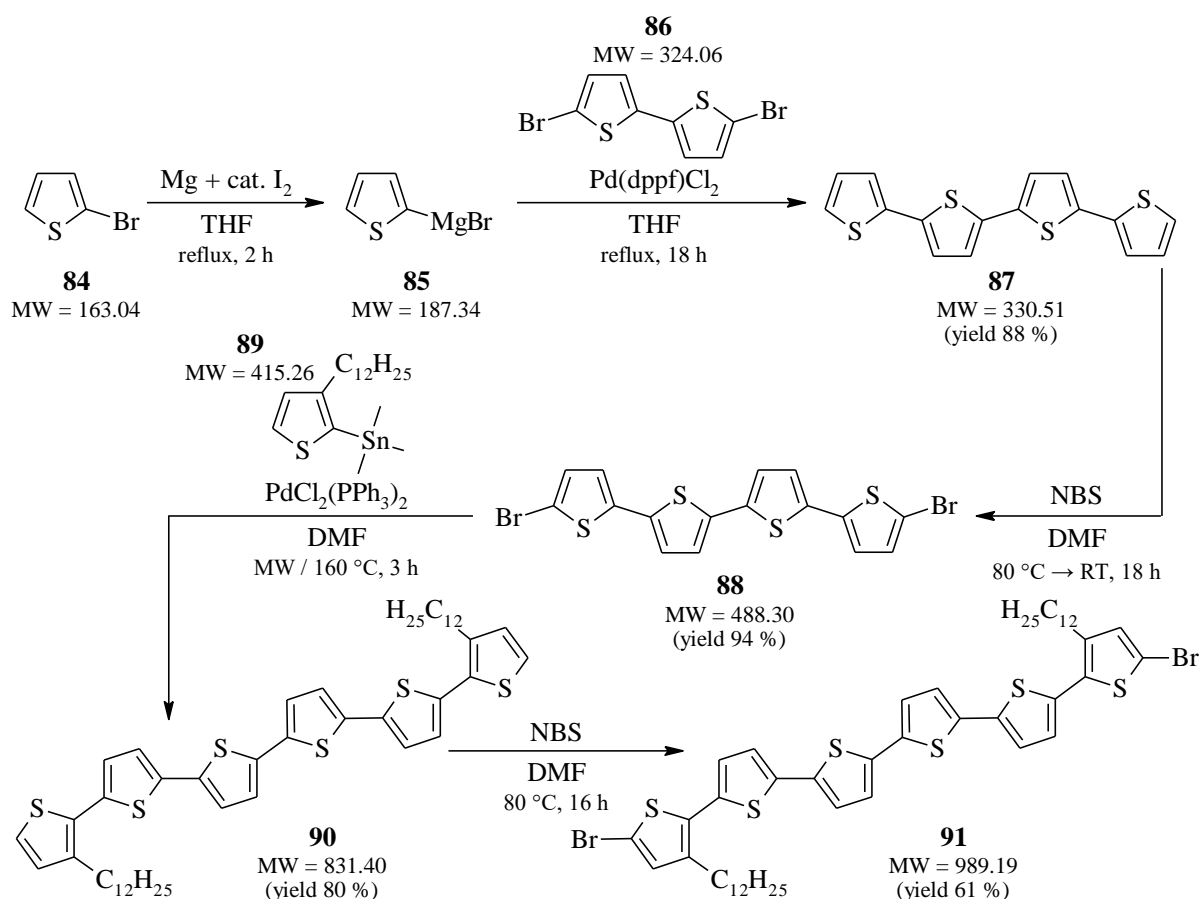
All three prepared *O,O'*-alkylated NTD derivatives will be studied from the point of view of optical and thermal properties. In particular, the contribution of adamantyl side chains and their effect on the resulting properties of the product will be studied and compared to other related compounds.

4.5 PREPARATION OF PT DERIVATIVE

4.5.1 Synthetic route to the key monomer based on sexithiophene

Since the final polymerization step was performed using *Stille cross-coupling* reaction, the key monomer for the preparation of the resulting polymer based on β,β' -dialkylated sexithiophene was its dibrominated derivative (**91**). Five steps of the synthetic route led to the preparation of **91** (**Scheme 24**), starting with 2-bromothiophene (**84**) and its conversion to the *Grignard reagent* **85** in a conventional way. **85** was subsequently used for the reaction with 5,5'-dibromo-2,2'-bithiophene (**86**) in the presence of a palladium^(III) catalyst by *Kumada cross-coupling* reaction to give quaterthiophene (**87**) in a great yield of 88 %. In the next step, **87** was brominated with NBS to give the dibromo derivative **88** in a yield of 94 %. **88** was used for the subsequent reaction with the already prepared *Stille intermediate* **89** to obtain β,β' -dialkylated sexithiophene (**90**) by *Stille cross-*

coupling reaction and using pulsed microwave heating in a high yield of 80 %. The previously discussed catalyst/ligand/additive mixture [Pd(OAc)₂/PPh₃/CuI] was also tested in this synthesis but did not lead to any product. The commonly used PdCl₂(PPh₃)₂ catalyst proved to be excellent. In the final step, bromination of **90** was performed with NBS to give the final target monomer **91** in a yield of 61 %. Both brominations in this synthetic approach required elevated temperature (~80 °C) and relatively high dilution due to the limited solubility of the starting polythiophene derivatives.



Scheme 24: Five-step synthetic route to the key monomer based on sexithiophene (**91**)

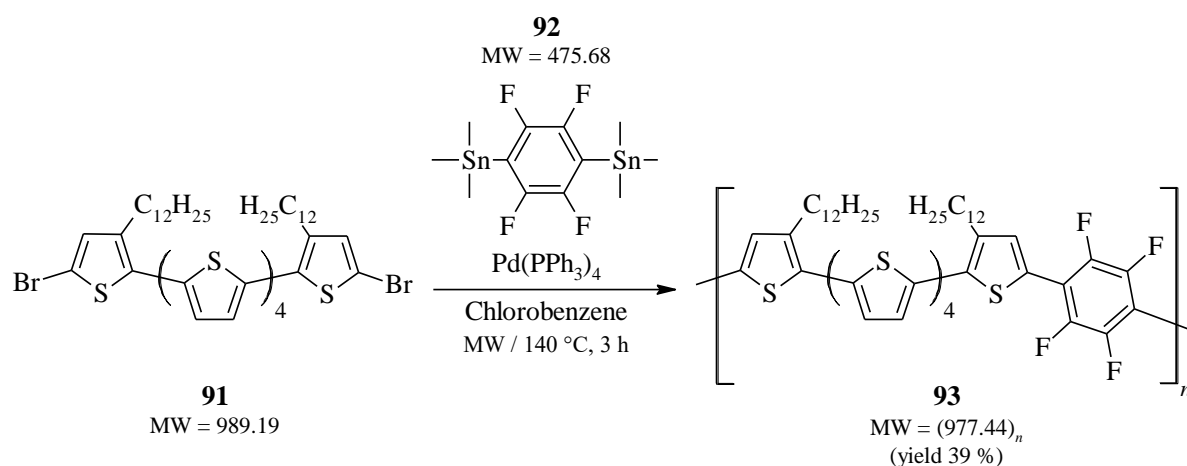
In summary, the resulting monomer **91** was prepared in an overall yield of 40 %, which is an excellent value since none of the steps was optimized. In addition, **91** is a novel derivative, not yet described in the literature.

4.5.2 Final polymerization to the targeted polymer (**93**)

As already mentioned, the final polymerization was performed by reacting the dibromo-derivative **91** with the *Stille intermediate* **92** by *Stille cross-coupling* reaction (**Scheme 25**). Numerous experiments have been performed in which various solvents (chlorobenzene, DMF, toluene) and catalysts [Pd(PPh₃)₄, PdCl₂(PPh₃)₂, a mixture of Pd(OAc)₂/PPh₃/CuI] have been tested. In all cases,

microwave heating of the reaction mixture with a pulse technique was used, the maximum temperatures being chosen according to the nature of the solvent.

The best polymerization results were obtained using a chlorobenzene solvent with a dilution of approx. 7 mg/mL and 5–6 mol% of $\text{Pd}(\text{PPh}_3)_4$ catalyst. The maximum heating temperature was set at 140 °C and the reaction time of one MW cycle was 3 h. It proved to be beneficial to repeat the MW cycle 1–2 times after the addition of another 5 mol% of catalyst. At best, polymer **93** was prepared with a narrow distribution of about 4 500 g mol⁻¹ in a yield of 39 %.



Scheme 25: Preparation of β,β' -didodecyl- α -sexithiophene-tetrafluorophenyl polymer (**93**)

The experiment was repeated many times and the target polymer **93** was prepared in moderate yields from 39 % to 65 % and with a sufficient degree of polymerization (MW \approx 4 100 g mol⁻¹ according to GPC) for the purposes of the following study of the optical, electrical as well as photovoltaic characteristics planned for this material.

5 CONCLUSIONS

The doctoral thesis deals with organic high-performance pigments applicable in the fields of organic electronics. The first part of the theoretical section of the thesis introduced the issue of organic electronics and photonics and the basic parameters that materials applicable in these areas must meet. Furthermore, a group of substances called organic high-performance pigments was characterized, and gradually selected groups of these substances (DPPs, BDFs, ID/IID/EPs, NTDs, PTs) were introduced. From each group, the most important derivatives showing exceptional properties in the fields of organic electronics were described, especially in terms of the transport characteristics in OFET devices, but also PCE in BHJ-SC devices. Moreover, the influence between the structure of derivatives and the resulting properties was briefly discussed. Therefore, the structures of individual derivatives subsequently served as inspiration for the own design of completely novel derivatives, potentially useful in similar applications. In the second part of the theoretical section, the synthetic possibilities of appropriate groups of derivatives and their most common structural modifications were described.

In the experimental part of the thesis, all performed experiments were described in detail. A total of 103 molecules were successfully prepared in this doctoral thesis, of which 54 were intermediates, and 49 were target products. Of the target products, 27 were completely novel, not yet described in the literature. On the other hand, the 14 experiments performed were unsuccessful and did not lead to the desired products.

In the following results and discussion section, the individual synthetic approaches were gradually evaluated. One of the main motives of the experimental part of the thesis was the incorporation of bulky adamantyl derivatives into the molecules of organic high-performance pigments and the study of their influence on the resulting properties. In particular, an in-depth study was performed on the series of *N,N'*-; *N,O'*- and *O,O'*-alkylated thiophene DPP derivatives by ethyladamantyl chains and for comparison 2-ethylhexyl's as the most commonly used alkylated DPPs in the literature. No comprehensive study describing their physicochemical properties has been published so far for these relatively overlooked derivatives. On the other hand, these are by-products, the formation of which must be considered in every alkylation of lactam groups by branched or bulky alkyl chains. Herein, 2 series with a total of 6 derivatives were prepared, on which the selectivity of alkylation, thermal properties and optical properties in both solutions and thin films were studied.

It has been found that the nature of the alkyl chains have a crucial influence on the formation of *N,N'*-alkylated products and with the increasing bulkiness of these substituents the ratio of *O*-alkylated products formed increases. Furthermore, it has been shown that *O*-substitution leads to a significant deterioration in the thermal stability of the resulting derivatives compared to *N*-substitution. On the contrary, the contribution of adamantyl chains proved to be distinctive, as it significantly increased the melting points and thermal stability of all 3 regioisomers in

comparison with 2-ethylhexyl derivatives. The obtained results were published in an impacted journal⁷³.

In the same trend, adamantane chains have been incorporated into a diverse range of other DPPs and also into the molecule of another representative of organic pigments, epindolidione. For the vast majority of these derivatives, the expected result of increased thermal stability and melting points due to the presence of adamantyl substituents was observed. Other physicochemical properties and especially the application potentials of these novel derivatives are further studied in detail, and the results will be published in the future.

Furthermore, a series of thioketo analogues of DPP derivatives (DTPPs) were prepared, both basic non-alkylated and substituted by alkyl chains on sulphur and nitrogen atoms. Detailed studies of the properties of all these derivatives are further in progress. Efforts have also been focused on the synthesis of a DPP derivative containing both adamantyl chains and strong electron-accepting dicyanovinyl groups in its structure, which should bring a significant improvement in the transport characteristics of the derivative based on published results discussed in the review section. However, this is a relatively demanding, multi-step synthetic route, which, unfortunately, was not completed for this doctoral thesis.

A series of *O,O'*-alkylated NTD derivatives containing bicyclic lactam groups analogous to DPP derivatives was also prepared using dodecyl, 2-ethylhexyl and ethyladamantyl chains. Studies of physicochemical properties and the study of their application potentials are also being carried out on isolated derivatives. The formation of *N,N'*-alkylated NTDs is minor compared to DPPs and in the case of *N,N'*-ethyladamantyl NTD, it was not possible to obtain a yield higher than 3.4 %. Unfortunately, the possibility of preparing this derivative by metal-free *O-* to *N*-alkyl migratory rearrangement using TfOH and DCE as solvent⁸³ has also failed.

Moreover, as part of this doctoral thesis, a completely novel, as yet undescribed polymer containing alternating units of β,β' -didodecyl-sexithiophene and tetrafluorobenzene was prepared. The study of physicochemical properties, especially in terms of the effect of π -conjugation prolongation of the monomer, is also in progress and the polymer application potential in photovoltaic devices is further investigated. The results should be published soon.

Unfortunately, the synthetic branch leading to thiophene analogues of BDF has so far proved unsuccessful, although the reference synthesis of the already described phenyl-BDF was successful. In the case of thiophene analogues of BDFs, both symmetrical unsubstituted or substituted by solubilising dodecyl chains, and asymmetrical, the structures of the resulting derivatives were not confirmed in any of the cases. Nevertheless, the isolated substances usually showed the character of an organic pigment, but the used structural analyses did not confirm the existence of the desired skeleton. It is very difficult to determine the exact cause of this failure; however, the obstacle was most likely in the structural analysis and not in the synthesis itself. This issue will be further intensively solved.

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7 LIST OF USED ABBREVIATIONS AND SYMBOLS

7.1 ABBREVIATIONS

| <i>abbreviation</i> | <i>meaning</i> |
|---------------------------------|---|
| AcOH | acetic acid |
| AHA | α -hydroxy acid |
| BDF | benzodifuranone (furo[2,3- <i>f</i>][1]benzofuran-2,6-dione) |
| BHJ-SC | bulk heterojunction solar cell |
| CHCl ₃ | chloroform |
| CO ₂ | carbon dioxide |
| Cs ₂ CO ₃ | caesium carbonate |
| CuCN | copper cyanide |
| CuI | copper(I) iodide |
| DCE | 1,2-dichloroethane |
| DMF | <i>N,N</i> -dimethylformamide |
| DMSO- <i>d</i> ₆ | deuterated dimethyl sulfoxide |
| DPP | diketopyrrolopyrrole (2,5-dihydropyrrolo[4,3- <i>c</i>]pyrrole-1,4-dione) |
| DTPP | dithioketopyrrolopyrrole (2,5-dihydropyrrolo[4,3- <i>c</i>]pyrrole-1,4-dithione) |
| EDG | electron-donating group |
| EIA | U.S. Energy Information Administration |
| EP | epindolidione (dibenzo[<i>b,g</i>][1,5]naftyridin-6,12(5 <i>H</i> ,11 <i>H</i>)-dione) |
| equiv. | an equivalent, the amount of a substance relative to another substance in the chemical reaction |
| EtOH | ethanol |
| EWG | electron-withdrawing group |
| FeCl ₃ | iron(III) chloride |

| | |
|--|--|
| GC-MS | gas chromatography-mass spectrometry |
| GPC | gel permeation chromatography |
| H ₂ O | water |
| HBr | hydrobromic acid |
| HCl | hydrochloric acid |
| HOMO | highest occupied molecular orbital |
| I ₂ | iodine |
| ID | indigo [(2 <i>E</i>)-2-(3-oxo-1,3-dihydro-2 <i>H</i> -indol-2-yliden)-1,2-dihydro-3 <i>H</i> -indol-3-one] |
| IID | isoindigo [(3 <i>E</i>)-3-(2-oxo-1,2-dihydro-3 <i>H</i> -indol-3-yliden)-1,3-dihydro-2 <i>H</i> -indol-2-one] |
| K ₂ CO ₃ | potassium carbonate |
| KOH | potassium hydroxide |
| LUMO | lowest unoccupied molecular orbital |
| Mg | magnesium |
| MW | microwave |
| Na | sodium |
| NaNH ₂ | sodium amide |
| NaOH | sodium hydroxide |
| NBS | N-bromosuccinimide |
| NMP | <i>N</i> -methylpyrrolidone |
| NMR | nuclear magnetic resonance spectroscopy |
| NTD | naphthyridinedione (1,5-dihydro-1,5-naphthyridine-2,6-dione) |
| O ₂ | oxygen |
| OECD | Organization of Economic Cooperation and Development |
| OFET | organic field-effect transistor |
| OLED | organic light-emitting diode |
| OPD | organic photodetectors |
| OPV | organic photovoltaics |
| OSC | organic solar cell |
| P(<i>t</i> -Bu) ₃ HBF ₄ | tri- <i>tert</i> -butylphosphonium tetrafluoroborate |
| PCE | power conversion efficiency |
| Pd(OAc) ₂ | palladium(II) acetate |
| Pd(PPh ₃) ₄ | tetrakis(triphenylphosphine)-palladium(0) |
| PdCl ₂ (PPh ₃) ₂ | bis(triphenylphosphine)palladium(II) dichloride |
| POCl ₃ | phosphoryl trichloride |
| PPh ₃ | Triphenylphosphine |
| PT | polythiophene |
| PtO ₂ | platinum oxide (Adams' catalyst) |
| TAA | <i>tert</i> -amyl alcohol |
| TfOH | triflic acid (trifluoromethanesulfonic acid) |
| THF | tetrahydrofuran |
| TLC | thin-layer chromatography |

7.2 SYMBOLS

| <i>symbol</i> | <i>meaning</i> |
|-----------------|--|
| \$ | dollar |
| °C | the degree Celsius, unit of temperature |
| g | gram, unit of mass [10^{-3} kg] |
| h | hour, unit of time |
| Hz | hertz, unit of frequency |
| kWh | kilowatt-hour, unit of energy |
| mg | milligram, unit of mass [10^{-6} kg] |
| mL | millilitre, unit of volume [1 cm^3] |
| mmol | millimole, unit of amount of substance |
| psi | pound-force per square inch, unit of pressure [6 894.757 Pa] |
| T_{MP} | melting point temperature [°C] |

8 CURRICULUM VITAE (CV)

PERSONAL INFORMATION

Name, Title: **Martin Cigánek, Ing.**
Address: Opletalova 403/26, 679 04 Adamov
Czech Republic
Date of birth, place: 18th September 1992 in Brno
Nationality: Czech
E-mail: xcciganek@fch.vut.cz

EDUCATION

2017 – present Brno University of Technology, Faculty of Chemistry
Programme: Chemistry, Technology and Properties of Materials
Level of course unit: Doctoral

2015 – 2017 Brno University of Technology, Faculty of Chemistry
Programme: Chemistry for Medical Applications
Level of course unit: Master's

2012 – 2015 Brno University of Technology, Faculty of Chemistry
Programme: Chemistry for Medical Applications
Level of course unit: Bachelor's

2004 – 2012 Grammar school Blansko (general)
Finished: The state graduation exam

EMPLOYMENT

03-2017 – present Materials Research Centre
Ph.D. student researcher in the Laboratory of organic synthesis

09-2013 – present Brno University of Technology, Faculty of Chemistry
Student researcher in the Laboratory of organic synthesis

03-2016 – 05-2020 HB Glass Ltd. – Technical section
Development engineer of new applications for glass systems

PEDAGOGICAL ACTIVITY

2019 – present Laboratory Classes in Organic Chemistry
Laboratory exercise, Czech

2018 – present Organic Chemistry II
Exercise, Czech

2017 – present Organic Chemistry I
Exercise, Czech

CONSULTATION/REVIEW OF FINAL THESES

| | |
|--------------------|---|
| 2019 – 2020 | Terézia Prekopová – Bachelor's thesis review Nature-inspired macro cyclic systems for bioorganic applications |
| 2018 – 2019 | Lucia Ivanová – Bachelor's thesis review Study of effect of side chains of organic semiconductors for bioelectronic applications |
| 2017 – 2018 | Kamil Mamleev – Bachelor's thesis consultation The synthesis and functionalization of diketopyrrolopyrrole derivatives for organic electronics |

DEVICES AND TECHNIQUES SKILLS

| | |
|--------------------|---|
| Practical | organic synthesis, microwave-assisted synthesis, nuclear magnetic resonance spectroscopy, gas chromatography, mass spectrometry |
| Theoretical | liquid chromatography, electrophoretic methods, UV-VIS spectrophotometry, thermal analysis |

LANGUAGES

| | |
|----------------|-------------------------------|
| Czech | native language |
| English | upper intermediate (level B1) |
| Spanish | basic knowledge |

OTHER SKILLS

| | |
|------------------------|---------|
| Driving licence | group B |
|------------------------|---------|

PUBLICATION ACTIVITY

Articles in impacted journals

CIGÁNEK, M.; HEINRICHOVÁ, P.; KOVALENKO, A.; KUČERÍK, J.; VALA, M.; WEITER, M.; KRAJČOVIČ, J. Improved crystallinity of the asymmetrical diketopyrrolopyrrole derivatives by the adamantane substitution. *Dyes Pigm.* 2020, **175**, 108141. DOI: 10.1016/j.dyepig.2019.108141

KOVALENKO, A.; VALA, M.; CIGÁNEK, M.; WEITER, M.; KRAJČOVIČ, J. Design rules for the large two-photon absorption diketopyrrolopyrrole-based quadrupolar symmetrical chromophores. *Chem. Pap.* 2018, **72**(12), 3033–3042. DOI: 10.1007/s11696-018-0530-7

Articles in indexed journals

CIGÁNEK, M.; HEINRICHOVÁ, P.; WEITER, M.; KRAJČOVIČ, J. Novel adamantane asymmetrically substituted diketopyrrolopyrroles. *EKC2019*. 2020.

Conference contributions

CIGÁNEK, M.; HEINRICHOVÁ, P.; KOVALENKO, A.; VALA, M.; WEITER, M.; KRAJČOVIČ, J. *Improved crystallinity of the novel asymmetrical substituted diketopyrrolopyrrole derivatives (DPPs) by the adamantane side chains*. 14th International Symposium on Functional π -Electron Systems (F π 14) Berlin (June 2–7, 2019). **2019**. p. 39–39.

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AWARDS

- 2019** Scientific Committee Award for oral presentation at the student scientific conference “*Chemistry Is Life 2019*”
- 2018** Award for young scientific talent within the student section of the International Scientific Conference “*Chemistry & Life 2018*”
- 2017** Scientific Committee Award for oral presentation at the student scientific conference “*Chemistry is Life 2017*”
- 2017** Dean’s Award for Master’s thesis
- 2015** Dean’s Award for Bachelor’s thesis

Brno 1. 8. 2020