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AUTOREFERÁT DISERTAČNÍ PRÁCE / SUMMARY OF THE PHD THESIS

PŘÍPRAVA MODULÁRNÍCH PRVKŮ PRO MOLEKULOVOU ELEKTRONIKU

SYNTHESIS OF MODULAR COMPONENTS FOR MOLECULAR ELECTRONICS

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1. Introduction

The rapid technological advances in electronics and computing that have occurred over the last half century are based on the progressive miniaturization of the components involved. The traditional approach to this is to start with something large and then to find ways to make it progressively smaller and smaller (top-down approach). It was predicted in 1965 by Gordon Moore, co-founder of the Intel Co., that there would be a doubling of devices per chip every 18-24 months.[1] This so-called Moore´s Law has held true over the past 45 years, however this approach will reach its physical limit in the next 10 -15 years due to certain limiting factors. The alternative is the bottom-up approach, where molecules are synthesized to possess some inherent function, then assembled with other components to build the electrical device.

In 1974, Aviram and Ratner theoretically proposed the concept of a molecular rectifying diode,[2] where an acceptor-bridge-donor molecule can play the same role as a semiconductor p-n junction and could be used as alternatives to silicon chips. Since that, many research groups have reported on the electrical properties of molecular-scale devices from single molecules to monolayers.

Molecular electronics can be defined as technology utilizing single molecules, small groups of molecules, carbon nanotubes, nanoscale metallic or semiconductor wires or polymers to perform electronic functions. Several recent reviews of the active field of molecular electronics are available.[3-8] For the construction of complex molecular electronic devices will be necessary to assemble the complicated objects from a limited set of rods, connectors, and other simple building elements. The concept of modular chemistry considers connection of the individual parts (modules) into fixed-shape molecular objects.[9,10] Modules are based on rigid or semi-rigid chemical compounds or groups with exactly defined size.[11] The modules can be bind together via self-organization/assembly, which takes advantage of the non-covalent interactions, i.e. hydrogen bonds,[12,13,14] or using covalent bonding.[15]

Many research groups are focused on the preparation of molecules and functional components, their assembling into well-defined structures and on the study of physical and chemical properties for the further applications in molecular electronics, material sciences and other fields of research.

2. Aims of the work

With regard to long-term interest of our group in the field of molecular electronics, the aim of this thesis were the syntheses and study of new modular systems derived from pyridinium, carborane, bicyclo[2.2.2]octane and (η^4-cyclobutadien)(η^5-cyclopentadienyl) cobalt derivatives. This overall objective includes several subtasks. For those it was necessary to develop a general methodology for preparation and separation of such compounds. The particular goals were:

1. To develop a suitable method for the preparation of pyridinium oligomers with well-defined lenght and to prepare a series of these oligomers terminated with different functional groups for further electrochemical and spectroscopic studies. To find a simple method for the preparation of pyridinium oligomers terminated on both sides with suitable alligator clips (alkylsulfanyl and acetylsulfanyl groups) for further conductivity, electrochemical and spectroscopic studies of these oligomers anchored between conductive gold electrodes.
2. To prepare a set of „molecular insulators“, which are based on derivatives of bicyclo[2.2.2]octane, 1,12-dicarba-*closo*-dodecaborane and 1,10-dicarba-*closo*-decaborane.
3. To prepare a set of „molecular diodes“ (D-I-A molecules), where the acceptor part, consisting of pyridinium oligomer, and the donor part, consisting of (η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl) cobalt complex, will be separated by a series of "molecular insulators“.
4. To study the possible use of symmetric square (η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl) cobalt complexes for the construction of various molecular devices, where these complexes can act as cross-shaped star connectors and such devices could operate as molecular sensors.
5. Preparation of self-assembled derivatives of (η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl) cobalt complexes, and study a possible substitution of cyclopentadienyl ring.

3. Results and discussion

3.1 Preparation of pyridinium oligomers

A convenient method for the preparation of pyridinium oligomers with defined length, based on the preparation of monofunctional units **4** resp. **6**, have been developed (*Figure 1*). [16]

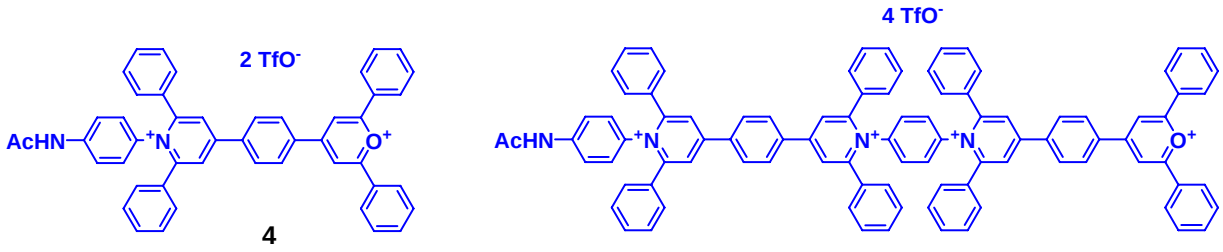
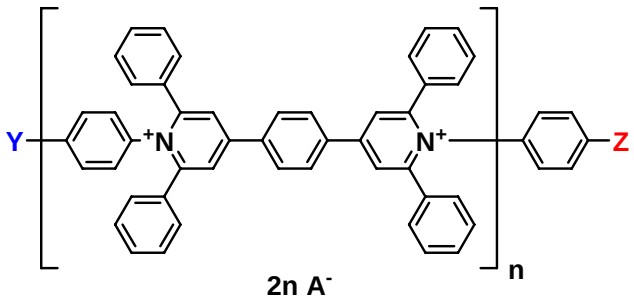


Figure 1

The general structure of some pyridinium oligomers and their numbering is shown in *Figure 2*.



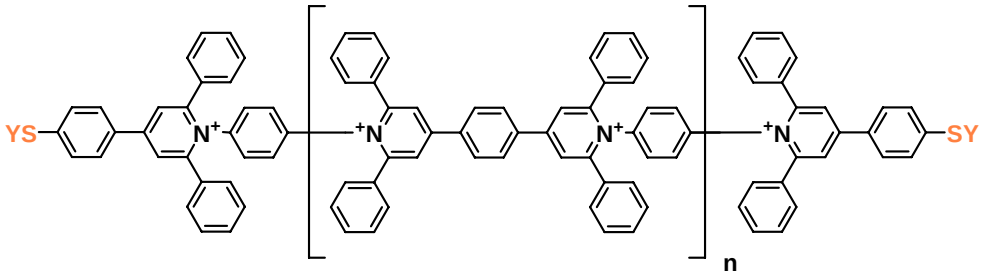
	Y	Z
0[n]	H	H
1[n]	NMe_2	NMe_2
2[n]	NH_2	NH_2
3[n]	NHAc	NHAc
4[n]	NH_2	NHAc
5[n]	Bpin	NHAc
8[n]	I	NHAc

Figure 2

Pyridinium oligomers **3[n]** (n = 1-5), terminating with acetamino group, were prepared by the reaction of "pyrylium-pyridinium" **4** or **6** with the amino groups of *p*-phenylenediamine, resp. monomer **2[1]** or oligomers **2[n]**. Thus prepared oligomers **3[n]** can be further hydrolyzed to the oligomers **2[n]**, terminated with amino group. Additional series of pyridinium monomers (**6[1]**, **7[1]**, **9[1]**), having terminal perfluorinated phenylene ring have been prepared for the further electrochemical and spectroscopic studies.

For conductivity studies of pyridinium oligomers depending on the length of the oligomer chain, pyridinium oligomers **10-13[n]** terminated with alkylsulfanyl resp. acetylsulfanyl groups were prepared as shown in *Figure 3*. Preparation of such oligomers is based on the preparation of

suitably substituted derivatives of pyrylium salts and subsequent reaction with the amino groups of *p*-phenylenediamine, respectively monomer **2[1]** or oligomers **2[n]** provided the desired oligomers.



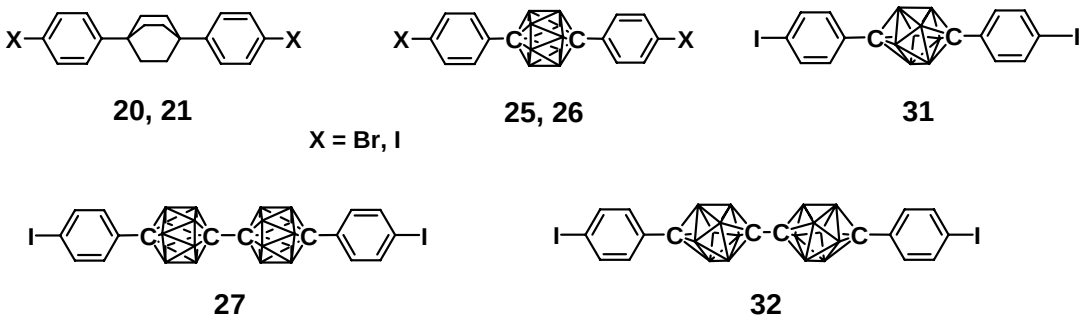
10-13[n]

Y= Me, Et, *tert*-Bu, Ac n=0-5

Figure 3

3.2 Molecular isolators

Several derivatives of bicyclo[2.2.2]octane **20**, **21**, as well as monomers and dimers of 1,12-dicarba-*closo*-dodecaborane **25-27**, and 1,10-dicarba-*closo*-decaborane **31**, **32** were prepared and used as molecular isolators (*Figure 4*). In choosing candidate structures for the "molecular isolators", we looked for saturated cage structures which are expected to have high ionization potential and low electron affinities, and also considered their synthetic accessibility.



20, 21 **25, 26** **31**

X = Br, I

27 **32**

Figure 4

3.3 Molecular diodes

In order to study rectification in single molecules, a series of monomolecular diodes **57-61** has been prepared (*Figure 5*). These molecular diodes consisted of pyridinium monomer as acceptor part and (η^4-tetraarylcyclobutadien)(η^5-cyclopentadienyl) cobalt complex as donor part. The donor and acceptor units were separated by the different molecular isolators. The methods for the

preparation and separation of the cobalt complexes have been developed and optimized, as well as the new method for a connection of the three different units of molecular diodes have been optimized. To compare the effect of an insulator spacer on the molecular rectification behavior of these substances, compound **56** was prepared, where the donor part is directly connected to the electron acceptor.

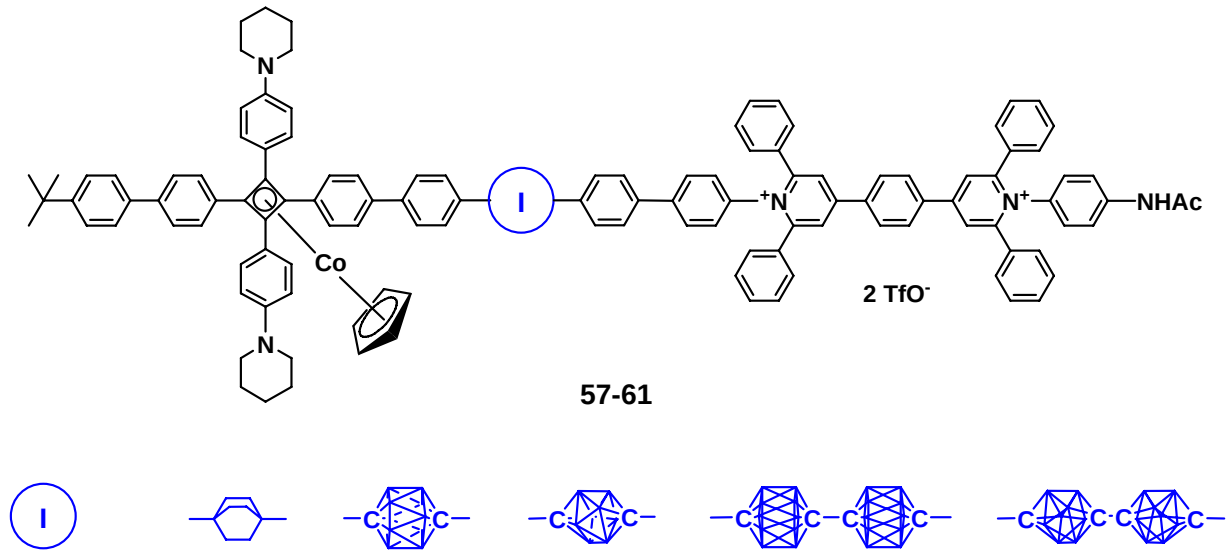


Figure 5

3.4 Molecular sensors

The set of molecular nanosensors has been prepared, where the cobalt complexes of cycobutadiene have been connected via an active center. These compounds could serve as the molecular chemical sensors, transistors (molchemFET) and logical networks, in which the conductivity is changed after complexation of the active center. As an "active sites" of nanosensores were used 1,10-phenanthroline, 2,2'-bipyridine, respectively and for the comparison of the conductivity changes after complexation of analyte (organophosphates, etc.), biphenyl. The metal complexes (Cu, W, Fe, etc.) of these "active sites" are known to have various degree of affinity for organophosphates, which are contained in organic fertilizers or in nerve agents (Sarin, Tabun,...). A series of dimers **76-84** have been prepared (*Figure 6*). For further conductivity measurements between gold electrodes, we are interested in molecules **79-84**, terminating with alkylsufanyl groups, but these molecules were prepared as a mixture of regioisomers, which had alkylsulfanyl groups in the horizontal and vertical positions. However the separation of mixtures of regioisomers

in the case of complexes (**79-84**) has failed. Only the complexes **76-78**, without alkylsulfanyl end groups, were prepared isomericaly pure.

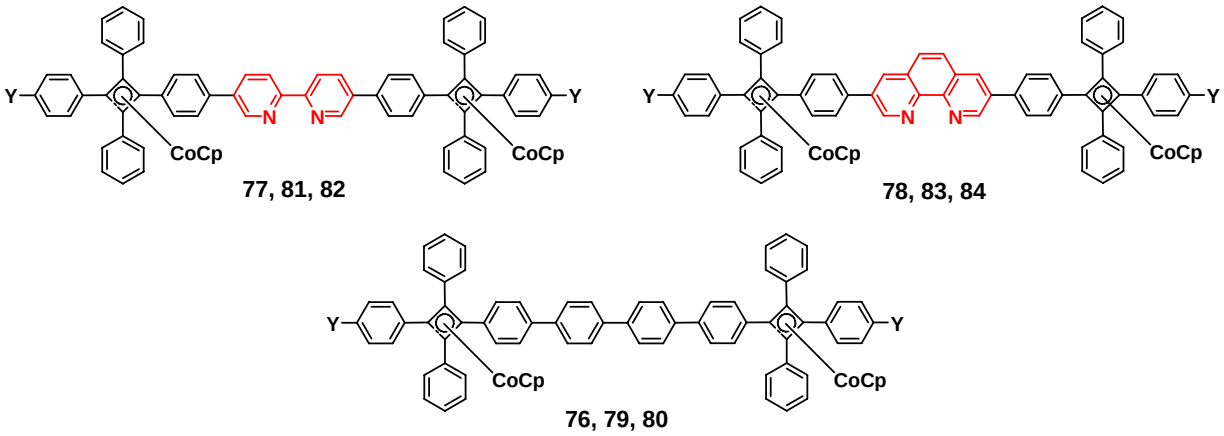
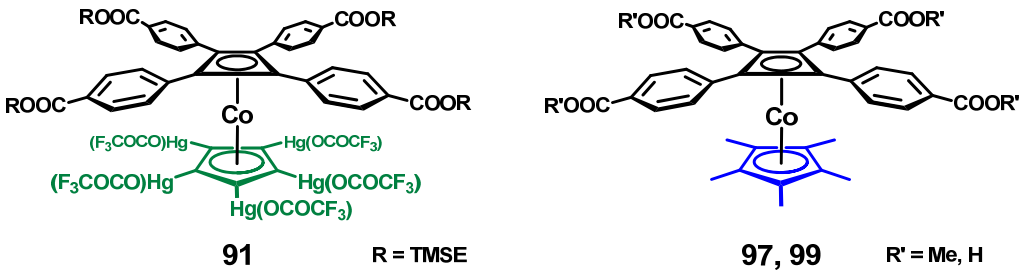


Figure 6

3.5 Self-assembled cyclobutadienyl cobalt complexes

Cobalt complexes with a suitably substituted Cp ring (permercurated) show affinity to the metal surface or mercury,[17,18] therefore tetraester complex **91** having pentakis (trifluoracetylmercury)cyclopentadienyl ring have been prepared. Several esters (*tert*-butyl, methyl and trimethylsilylethyl - TMSE) as protecting groups for carboxylic acid have been used. Only in the case of trimethylsilylethyl ester, the desired tetraester was prepared. After anchoring the cobalt complex to the metal surface, the ester is relatively easily removed with TBAF to get the free tetracarboxylic acid. This compound will be further used to study the self-assembly of the cobalt complexes on the metal surfaces.



Other cobalt complexes **97** and **99** with pentamethylated Cp ring have been prepared for further possible applications of the self-assembled square symmetric tetracarboxylic cobalt

complexes on various modified surfaces (peralkylated silicon, metal oxides, etc). The preparation of the complex with pentaallylated Cp ring, which could be further functionalized, has failed.

3.6 Physico-chemical studies of molecular electronics components

The derivatives prepared above would serve as functional elements in molecular electronic devices especially as molecular wires, diodes, sensors, or self-assembled components. For understanding their properties the series of physical-chemical studies have been measured in collaboration with the University of Colorado at Boulder, at Brookhaven National Laboratory (Upton, USA) and UFCH JH AVČR. Pyridinium oligomers have been extensively studied as a candidate for conductive molecular wire. In the oligomers, the extended viologene units are separated by aromatic rings twisted out of plane, which partially interrupt conjugation and make it likely that the transport of an electron that has been doped into the molecular wire will occur by hops from a unit to its neighbors.[19] These extended viologen unit accepts an electron in a fast and reversible process, yielding the cation radical, in which the added electron is fully delocalized. The cation radical has been generated and studied by pulse radiolytic, electrochemical, redox titration, UV-vis, IR and EPR spectroscopic methods.[20,21,22,16] All results are in agreement with a fully delocalized electronics structure. The pyridinium oligomers appear worth investigation for possible use as *n*-semiconducting molecular wires. Interesting results were achieved in the study of solubility of these oligomers, depending on the choice of anion.

Other functional molecular electronic devices (wires, diodes, sensors and insulators) are and will be further studied in the collaborating institutions. Measurements of these complex molecules are very complicated and require detailed study and more time than initially expected. These studies are in progress.

4. Conclusion

This work is focused on synthesis of new modular components (molecular wires, insulators, diodes, sensors and self-assembled compounds), which may find application in molecular electronics.

In the first part of this work (Chapter 4.1), procedure for the preparation of "molecular wires", based on the oligomers of pyridinium salts, is described. The synthetic strategy is based on a stepwise prolongation of these rodlike molecules by reaction of terminal amino group with the monofunctional unit **4** or **6.** The series of pyridinim oligomers **2[n]** and **3[n]** (where n = 1-5) of well defined length have been prepared without complicated separation of complex mixtures of oligomers. Also other pyridinium monomers **0[1]**, **1[1]**, **4[1]** and **5-9[1]** with different ending groups were prepared, which are then used to connect to other functional components using Suzuki coupling (**5[1]** and **8[1]**), or for further electrochemical studies of the influence of terminal groups and different substitution on the redox properties of pyridinium unit (**0,1,4,6,7,8,9[1]**).

The following part of work (Chapter 4.2) describes synthetic approach for the preparation of pyridinium oligomers ending with alkylsulfanyl **10-12[n]** or acetylsulfanyl **13[n]** groups. Synthesis of oligomers is based on the preparation of suitable substituted pyrylium salts **14-17** which were reacted with amino groups on both ends of the previously prepared pyridinium oligomers **2[n].** These compounds are further used to study the conductivity of conjugated oligomers, after anchoring between the gold electrodes.

The following section (Chapter 4.3) deals with the preparation of "molecular insulators" based on a rigid bicyclo[2.2.2]octane (**20**, **21**), 1,12-dicarba-*closo*-dodecaborane (**25-27**) and 1,10-dicarba-*closo*-decaborane (**31**, **32**) units. In the case of *p*-dicarba-*closo*-carborane derivatives, the monomers and dimer were prepared for the further study.

The next part (Chapter 4.4) deals with the preparation of a series of five „molecular diodes“ **57-61**, where the acceptor part (pyridinium monomer) and donor part [(η^4-tetraarylcyclobutadiene)(η^5-cyclopentadienyl) cobalt complex] are mutually separated by a series of „molecular insulators“.

The following section (Chapter 4.5) deals with the preparation of cross shape derivatives of (η^4-tetraarylcyclobutadiene) (η^5-cyclopentadienyl) cobalt complexes **73-75**, which were linked through the active part, which was either 1,10-phenanthroline or 2,2´-bipyridyl unit. A series of molecular sensors **76-84** has been prepared, but only unsubstituted dimers **76-78** were isomericaly

pure. The separation of regioisomeric mixtures of dimers **79-84**, functionalized with alkylsulfanyly group, has failed.

In the last section (Chapter 4.6) the preparation of self-assembled derivatives of (η^4-tetraarylcyclobutadien)(η^5-cyclopentadienyl) cobalt complexes **91**, **97**, **99** is described and possible substitution of cyclopentadiene ring was discussed.

The separate part (Chapter 4.7) is focused on the physico-chemical properties of the prepared compounds. Pyridinium oligomers have been studied using a variety of spectroscopic (pulse radiolysis, UV, IR, NIR, EPS) and electrochemical methods. All other derivatives (molecular wires, isolators, diodes, sensors, etc.) are studied in collaboration with other research laboratories (Boulder, Brookhaven, Prague).

About 121 new compounds were prepared in several series during the course of this work. Structures of all prepared compounds were established by combination of NMR techniques, mass and infrared spectroscopy or elemental analysis. Some results have already been published.[16,20,21,22,23]