Ground State Quinoidal Zwitterions as Molecular Tools

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Abstract

The PhD thesis outlines the idea of joining the chemistry of zwitterions as small molecules and as polymers in order to combine and to compare their properties at the molecular and polymeric level. Our approach is unique because it allows a control of the electronic properties based on the introduction of a tailored zwitterions, a crucial parameter in term of combined properties. The foundation of the approach comes from the precise control of the properties of the zwitterion, as a crucial factor. As these two fields are brought together certain objectives on each side must be achieved. There are two major milestones regarding the thesis:

1) To push further the known boundaries of the quinoidal zwitterion through:
- Insertion of new N-substituents (**Chapter 3**);
- Synthesis of C-substituents zwitterions to tune the electronic properties through the oxonol unit. (**Chapter 4**)

2) Exploring the possibilities of incorporating zwitterions in polymer chemistry (**Chapter 5**).

The first two chapters of the manuscript aim to familiarize the reader with the history, potential and behavior of the quinoidal zwitterions (**Chapter 1**) and explain the gap that they are filling in the complex world of macrocycles (**Chapter 2).**

Chapter 1. Chemistry of 12π electron quinones

Quinones have proven to be an interesting subject of research for the past decades. The 1,4-benzoquinone or p-benzoquinone is the main body of these compounds which are strongly present in:

- biological processes (photosynthesis : plastoquinone[1], phylloquinone[2])
- organic synthesis (oxidation agent : 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone),
- industrial use (E120: carmine, E130: indanthrone blue)

- drug industry for example as anti-cancer drugs[3] and many other branches of chemistry such as coordination chemistry[4] (Figure **1**).

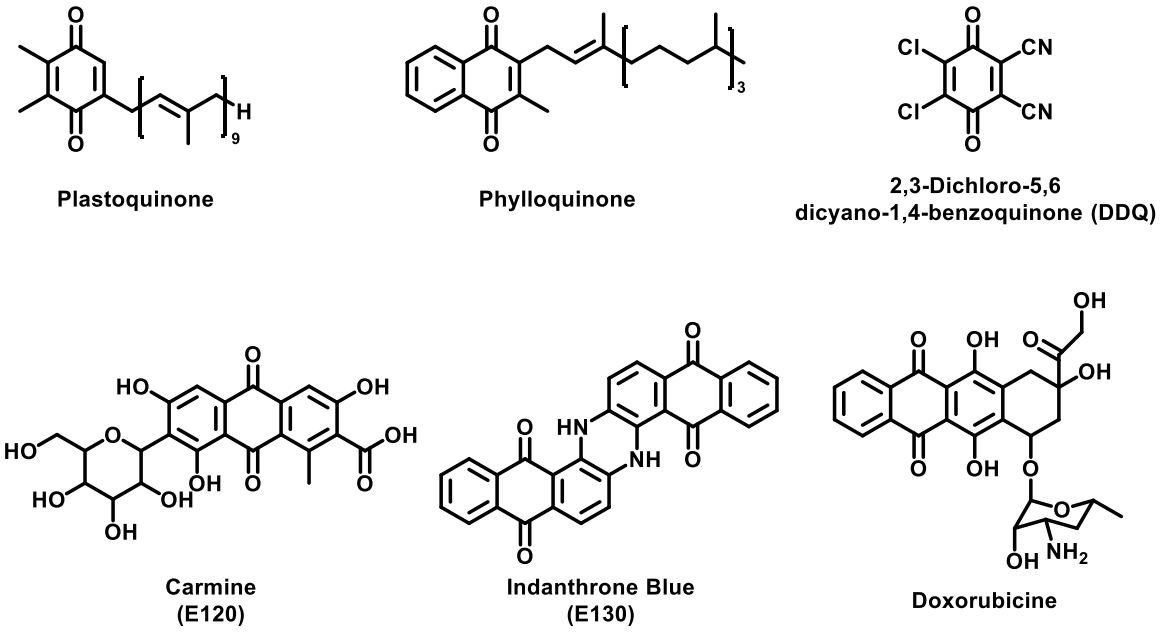


Figure **1**: Structure of several quinones

Starting from the quinone structure (Figure **2**) different architectures can be achieved through the introduction of different substituents on the remaining free positions of the ring. For the classical para benzoquinones, the electron delocalization takes place mostly on the two double bonds because of the cross-conjugation[5] effect which is responsible for the non-aromatic character of these molecules. The insertion of heteroatoms bearing free electron pairs in position 2 and 5 will enrich the system leading to a total of twelve electrons forming what we know today as 12π electron quinones. The insertion of hydroxyl and/or amino groups in position 2 and 5 will drastically change the conjugation pathway as well as the properties of such compounds. All these features were first predicted then proven experimentally much later.

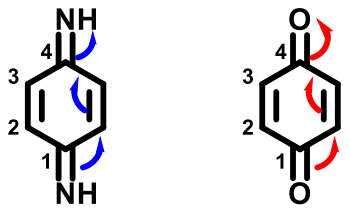


*Figure **2**: Delocalization of para benzoquinones*

Among the numerous quinones from literature, there are four main 12π electron quinones (Figure **3**). The differences between these quinones consist in the nature of the heteroatoms they contain and their relative position within the molecular structure. 2,5-Dihydroxy-[1,4]-benzoquinone (**A1**) contains four oxygen atoms in contrast to the diamino benzoquinonediimine (**A2**) which contains four nitrogen atoms in its structure. Different combinations containing both heteroatoms are also possible. Although both diamino benzoquinone (**A3**) and benzoquinonemonoimine (**A4**) contain two nitrogen and two oxygen atoms the difference in this case is given by their position within the molecule. In the case of diamino benzoquinone (**A3**) the oxygen atoms are found in position 1 and 4 and the nitrogen atoms in positions 2 and 5 or para position while in the case of benzoquinonemonoimine (**A4**) the atoms are found in meta position (Figure **3**).

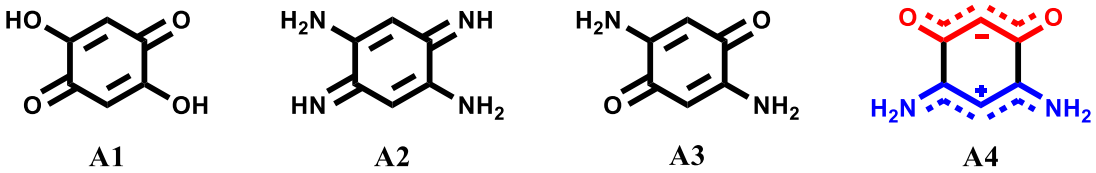


*Figure **3**: Structural difference of quinones*

In 1966 Dähne and Leupold theoretically predicted the coupling principle[6,7] of π-conjugated structures. This phenomenon takes place between two heteroatoms who belong to the IV, V or VI groups and connected through an odd number of sp^2 hybridized carbon atoms. This principle came as an answer to the unique optical properties of dyes containing coupled polymethine or oxonol units. The main characteristics of the compounds which meet the criteria for the coupling principle are: **1)** strong absorption of light at long wavelengths and **2)** the bond length within the polymethine chains should become largely equalized.

Specifically for the **A1** and **A2** quinones the dianionic and respectively the dicationic delocalized zwitterions have been isolated as well as their intermediates with only one side being delocalized. Using a tetrasubstituted diamino benzoquinone diimine (**DABQDI**) derivative of **A1** as an example we can observe the drastic color change dependence on the pH going from yellow to red for the monoprotonated species and to blue for the diprotonated form (Figure **4**). Following the results obtained with the help of x-ray diffraction it could be clearly seen in A13a structure an alternation between simple and double bonds. Upon protonation examination of the bond length in the **DABQDI H+** reveals the absence of this alternation on one side of the molecule having incorporated

one localized side and one delocalized. Finally, the diprotonated species **DABQDI 2H+** reveals two fully delocalized 6π subunits bridged by two pure σ bonds[8].

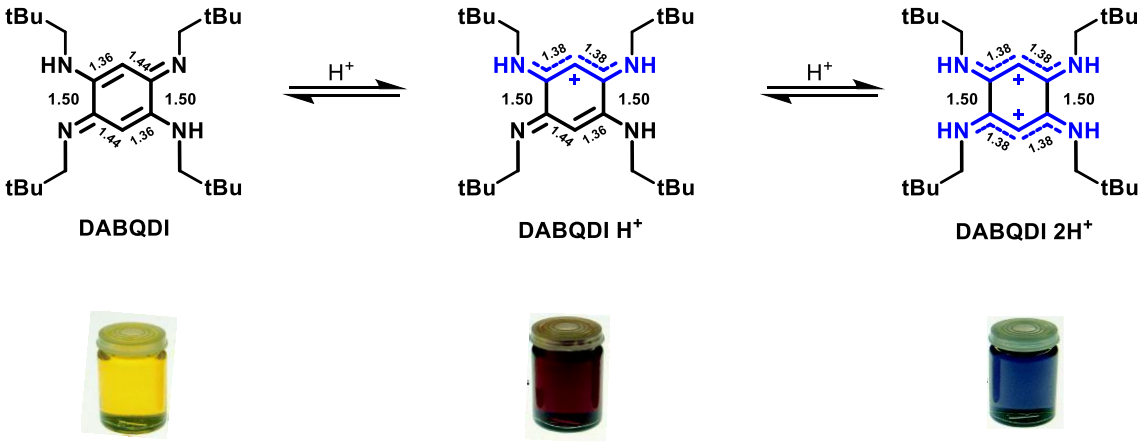


Figure **4:** Protonation stages of tetrasubstituted quinone **A1**

Unlike the exemplified quinones (A1 and A2) the benzoquinone monoimine zwitterion (BQMI) is found in its ground state already as a zwitterion without needing protonation/deprotonation. This very interesting structure is comprised of two (6+6)π delocalized subunits the trimethine oxonol and the trimethine cyanine chemically connected through simple carbon – carbon bonds, but electronically independent from each other.

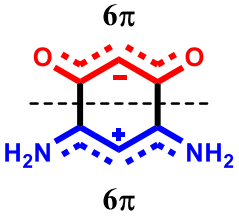


Figure 5: Illustration of Coupling principle of 6+6 π electrons in BQMI zwitterions

Chapter 2. Macrocyclic Compounds

Macrocyclic compounds represent a fascinating and diverse part of organic chemistry characterized by different aspects of their structure such as cavity size, chemical composition and structure which ultimately lead to unique properties.

Considering the dimension of this particular field there are only few significant macrocycles that inspired the formation of new macrocycles incorporating a **BQMI** zwitterion: **1)** calixarenes and **2)** cyclam.

2.1. Calixarenes

The chemistry of this class of macrocycles has been extensively studied since its discovery in 1963 when the x-ray crystallographic analysis was published for the first time[9]. Since then, the structure of calixarenes has changed either by changing the nature of the atom bridging the phenyl rings or by increasing the cavity size. These atoms could vary from the classical calixarene (bridged through carbon atoms) and azacalixares (bridged through nitrogen atoms) to thiacalixarenes[10] bridged by sulfur atoms and oxacalixarene bridged by oxygen atoms[11](Figure **6**).

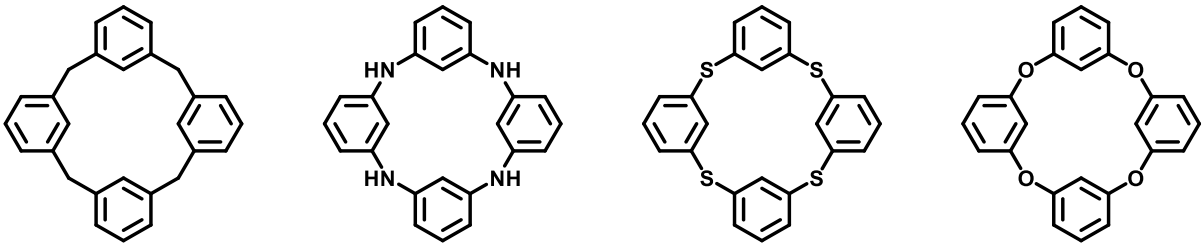


Figure **6**: General structures of calixarenes bearing different heteroatoms

Particularly interesting for our subject of research are the azacalixarenes which possess nitrogen atoms linking the four aromatic rings that have great potential in the host-guest chemistry.

Their capacity to act as host comes from their particular traits, since the cavity size, shape and different chemical groups can be attached to the cage.

One particular study revealing the importance of various parameters belongs to Casnati et al[12] where calixarenes of different dimensions varying from 6 to 8 member rings where modified with amide ionophores on both upper and lower rim for nuclear

waste removal. The results showed that some of the synthesized calixarenes had very promising results in regard to their retention potential for specific metal ions while others had no binding ability at all.

2.2. Cyclam

First discovered in 1936 by Jan van Alphen while trying to synthesize aliphatic polyamines, the cyclam macrocycles were obtained during the reaction between 1,3-dibromopropane and an excess of ethylenediamine. The reaction took place in alkaline pH using absolute ethanol as solvent. Upon the addition of copper (II) salt in the aqueous solution the complex formed had a red-violet color different from the usual blue color that has been observed. A part of the isolated compound was mixed with benzaldehyde and no reaction occurred suggesting of a compound with only secondary amines[13](Figure **7**).

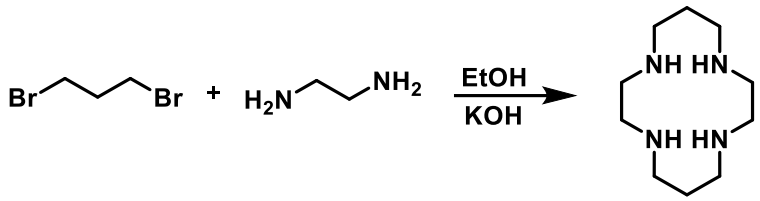


Figure **7**: Synthesis path developed by Jan van Alphen[110]

Similar to calix[n]arenes, cyclams macrocycles are not found in nature but due to several aspects such as ligand stability for complexes and its biocompatibility they are good candidates for biological applications such as antifungal agents[14].

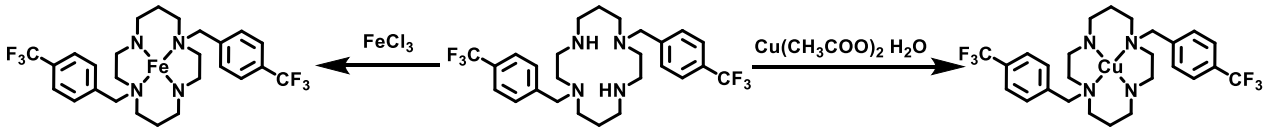


Figure **8**: Synthetic routs for cyclam complexes[113]

The development of pathogens with increased resistance is very frequent hence the need to develop novel compounds to inhibit several pathogens. The investigation of the antifungal activity of iron and copper complexes (Figure **8**) showed a higher efficiency for the iron complex.

Other complexes containing zinc, nickel, copper and many other metal centers have been reported in various medical applications such as HIV inhibitor and radiopharmaceuticals[15] proving the versatility brought by this class of macrocycles.

Chapter 3. Synthesis of novel BQMI macrocycles

In the literature there are several ways to synthesize **BQMI** zwitterions[16–18] but for this particular study we focused mainly on two approaches (Figure **9**).

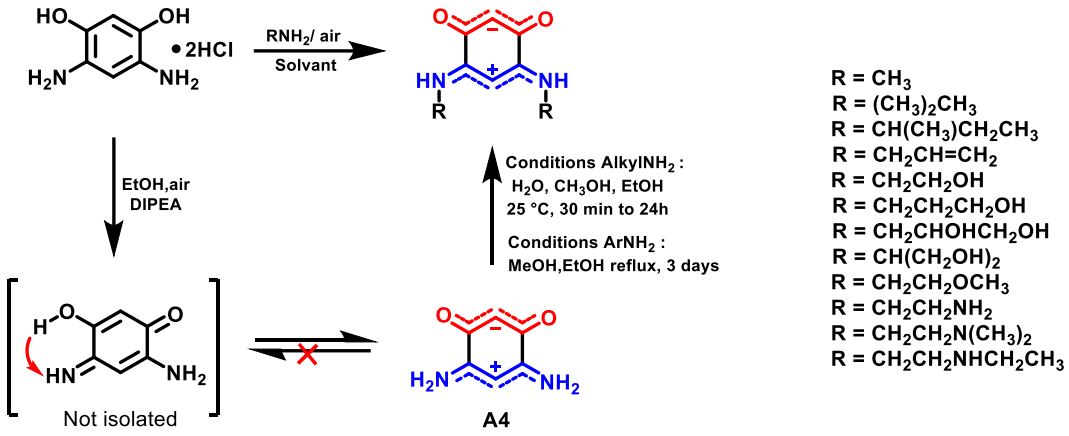


Figure **9**: Synthesis of transaminated zwitterions

Starting from 4,6-diaminoresorcinol dihydrochloride and by mixing it with N,N-diisopropylethylamine resulting A4 through intramolecular proton transfer in the presence of air. Further we can use A4 and the desired amine in order to obtain a transaminated zwitterion or we could use 4,6-diaminoresorcinol dihydrochloride and the desired amine in order to obtain the same transaminated zwitterions. The advantage of the isolating first A4 are the difficulty of purification and the yields that change.

The key takeaway here is that almost all transamination reactions were performed with primary amines, so the personal contributions of this chapter explore the reaction of **A4** zwitterions with polyamines[19].

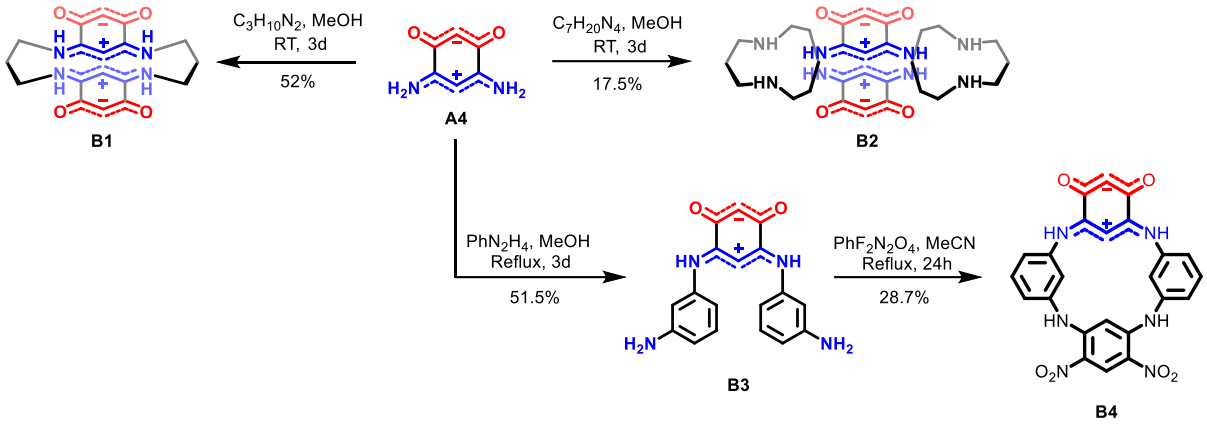


Figure **10**: Transamination of **A4** with diamines

The initial attempt in regard to **B2** was to try to imitate the cyclam structure by having one long polyamine chain react with both sides of the zwitterion. Through serendipity we discovered that instead of obtaining a classical zwitterion we isolated a macrocycle incorporating two zwitterionic cores and we proved that it can be achieved with smaller diamines such as propylene 1,3 – diamine by isolating **B1**.

Previously in the literature the para phenylenediamine substituted zwitterion[20] was isolated but there was no success in forming a macrocycles given the poor nucleophilicity of the free amine group. Instead **B3** was synthesized with the meta-phenylenediamine for better nucleophilicity but even so we could not isolate a symmetrical azacalixarene incorporating two zwitterionic cores due to the high amounts of reagents needed. As a result, we closed the ring with another reagent more electrophile 1,5 – difluoro – 2,4 – dinitrobenzene thus obtaining **B4**.

In conclusion three new macrocycles were synthesized two of which were obtained through one pot reactions with alkyl diamines while the azacalixarene zwitterion was obtained in two steps reactions.

Chapter 4. C-substituted zwitterions

The transamination reaction has been the keyway of tuning the properties of **BQMI** zwitterions. It has been the source of diverse structures remaining to this day the primary way to obtain different architectures containing the **BQMI** ring and as seen in **Chapter 1** much is yet to be discovered. The core property which has attracted attention over this molecule for the past two decades arises from the delocalized two 6π units incorporated in the six-member ring.

The focus of this chapter is expanding the class of **BQMI** zwitterions by introducing new substituents on the polymethine oxonol central carbon atom (C substitution) while preserving the delocalization.

Such compounds have been isolated in the past through the Michael reaction by using electron acceptors such as tetracyanoethylene (TCNE) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [21,22].

Similar to the approach presented in the literature bromo and iodo succinimides were used to obtain C-substituted zwitterions (Figure **11**).

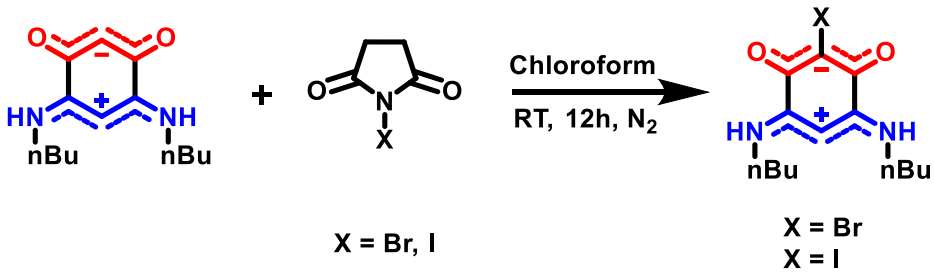


Figure **11**: Synthesis of C-substituted halogenated **BQMI**

Although this approach is reliable it does not provide the flexibility the transamination reactions provide. After searching the literature we discovered that we could use 2,5-dihydroxy-1,4-benzoquinone (**A2**) to obtain transaminated C-substituted zwitterions[23,24]. In order to synthesize asymmetrical C-substituted 2,5-dihydroxy-1,4-benzoquinones reactions with several steps and low yields are required. To overcome this issue embelin was extracted through Soxhlet extraction in chloroform[25].

After extraction embelin was mixed with N-butyl amine under reflux resulting in a C-substituted transaminated zwitterion which was furtherly used as a starting material to synthesize transaminated zwitterions (Figure **12**).

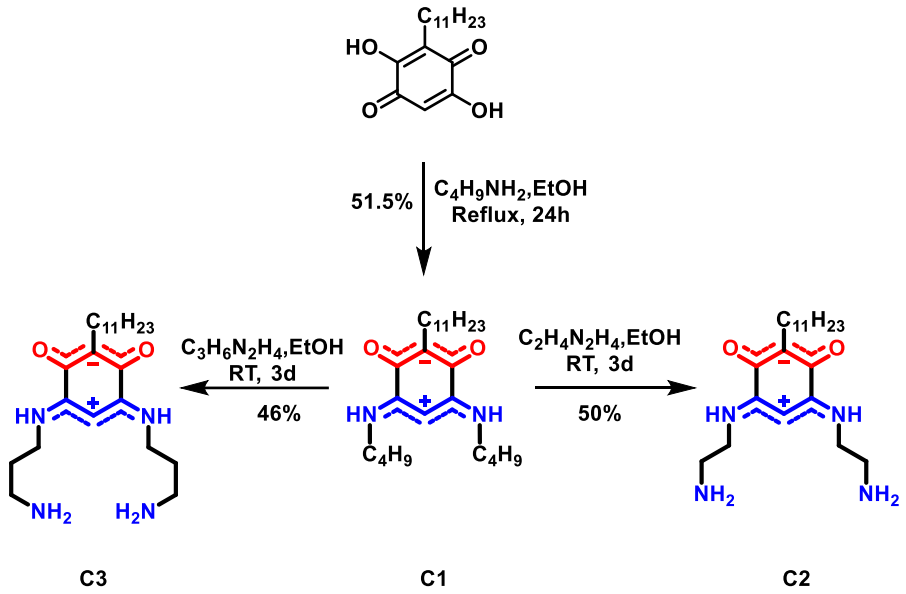


Figure **12**: Synthesis of C-substituted transaminated zwitterions

From an application point of view the **BQMI** zwitterions are well known in the literature for their potential as ligands as well as the applications[26–28] the resulting complexes can have[27–30]. Out of all possible combinations we chose to investigate the potential of nickel (II) complexes due to their capabilities of undergoing different geometries in solution and/or solid state. This change from planar geometry to octahedral helps close the gap between different orbital layers. Once the orbital potential difference becomes small enough the electrons rearrange themselves by filling each vacant space of the previously unoccupied orbitals which results in a change of spin which is further translated in the color change. The new synthesized complexes can undergo both solid state vapochromism and liquid state. One major difference is the substances with which the compounds complexate. The first trials were done with methanol and tetrahydrofuran, but we could register only a dilution through UV-Vis, and no color change was noticed. For this reason, stronger donors such as ammonia and pyridine were used. When drops of ammonia 28% or pyridine were added the orange solution upon shaking would turn instantly colorless (Figure **13**).

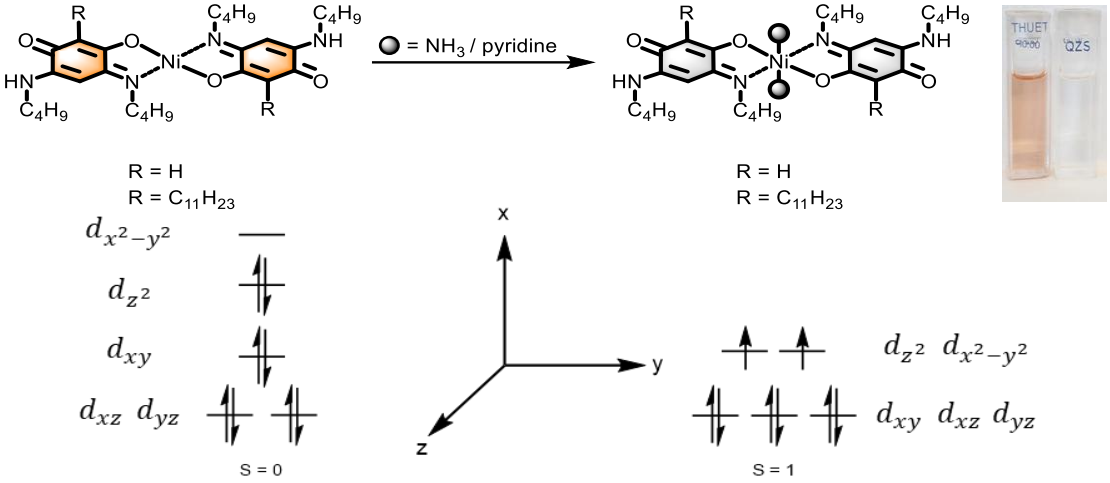


Figure **13**: Qualitative representation of the spin states of Ni(II) in square planar and octahedral environments

In order to prove that the change in color is caused by the complexation of pyridine, a titration study was performed, each curve being registered after adding 50µL of 10^{-3} or 10^{-2} M solution of pyridine in the tetrahydrofuran solution of 10^{-5} M.

Upon titration the energy band responsible for the product color in solution is slowly diminishing, while increasing the main absorption band at 352 nm reason why the solution is colorless (Figure **14Error! Reference source not found.**). Both C7b and C8b undergo same process while being titrated with different concentrations of pyridine. Upon titrating with a solution of 10^{-5} M or 10^{-4} M the only thing observed was a dilution. Increasing the concentration of the pyridine solution to 10^{-3} M for C7b and 10^{-2} M for C8b only 1 mL was necessary to obtain a colorless solution. It is worth mentioning that this process is fully reversible. After the complete evaporation of the solutions from the

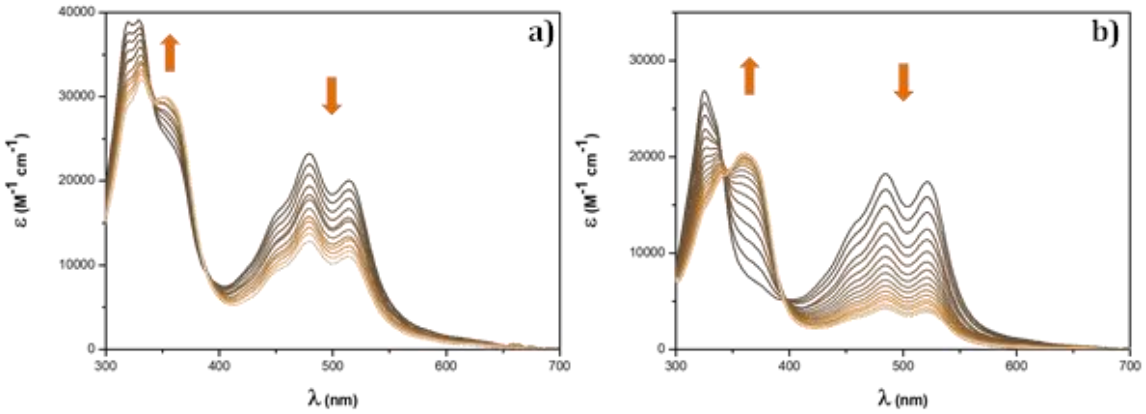


Figure **14**: Addition of 50 µL pyridine solution a) **C7b** 10^{-3}**,** b) **C8b** 10^{-2} in tetrahydrofuran at 10^{-5} M

cuvettes, the resulting precipitate was resolubilized resulting in the same orange colored solution.

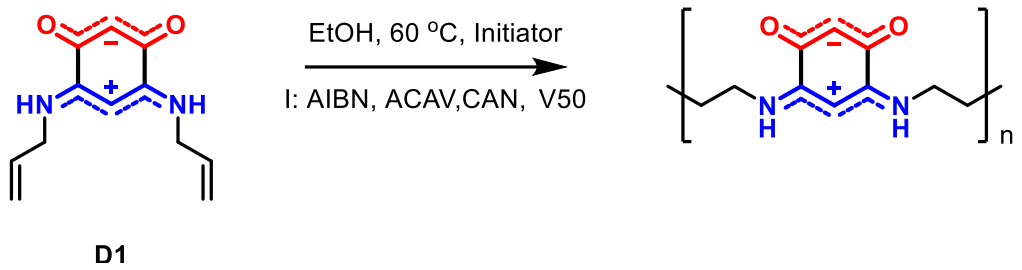
Chapter 5. Polymers incorporating zwitterions

The chemistry of the BQMI zwitterion **A4** has been intensively studied during the past two decades but these studies were focused mostly around the organic synthesis branch of chemistry. One of the three main objectives of this thesis was to push the boundaries of these molecules into the field of polymers while also maintaining the zwitterionic core in order to preserve the interesting characteristics of this class of molecules.

In order to do so two approaches were considered. The first one was to use the transamination reaction in order to introduce polymerizable groups and then further use the resulting molecule as a monomeric unit in a radicalic polymerization reaction[31]. This type of polymerization was chosen since it does not require any pH modifications which would allow us to keep the zwitterionic character of the molecule intact. The second approach consists in using commercial polymers that would contain free amine groups and chemically modify them with the classical **A4** zwitterion in order to obtain polymers that would incorporate the zwitterionic core.

The first attempts to obtain polymers started from a BQMI zwitterion bearing allylic double bonds. It is well known in the literature that the polymerization of allylic monomers is more challenging compared to the vinylic ones. This is because of the difficulty and downsides that comes with the stability of the double bond. Usually, the polymerization of allylic monomers results in products with a low degree of polymerization (oligomers) which is attributed to the degradative monomer chain transfer[32,33].

In the attempts to form a polymer starting from the zwitterion **D1** four different initiators were used: azobisisobutyronitrile (AIBN)[34], 4,4-azobis (4-cyanovaleric acid) (ACVA)[35,36], cerium (IV) ammonium nitrate (CAN)[37] and 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V50)[38] (Figure **15**).



D1

Figure **15**: Polymerization attempts of **D1** zwitterion

Since all the polymerization attempts failed instead of pursuing further this approach an alternative path was needed. Given the fact that the main issue is the stability of the allylic double bond I have attempted to insert a more reactive double bond.

This chemical modification was approached from two different ways. First through the classical transamination reaction using 4-aminostirene and 3-aminoethyl imidazolium bromide. The styrene is known to polymerize through different mechanisms[39] while the vinyl imidazole monomers are known to be able to polymerize through radicalic polymerization with AIBN reason why it was chosen[40] (Figure **16**).

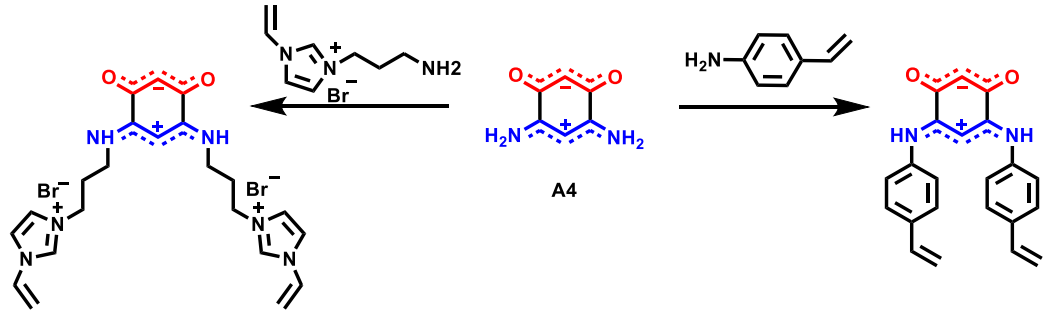


Figure **16**: Modification attempts for new monomers

Unfortunately, the two modification attempts were unsuccessful most likely due to the poor nucleophilic character of 4-aminostirene which is crucial for the transamination reaction or due to the steric hindrance in the case of the 3-aminoethyl imidazolium bromide. After several failed attempts to insert more reactive double bonds that could polymerize the only available approach from a synthesis point of view was to use polymers bearing free amines that could react with the zwitterion **A4** in order to form polymers incorporating the zwitterionic core.

Instead of using zwitterions as monomers commercial polymers such as polyallylamine hydrochloride with a Mw: 17.500 Da (Figure **17**).

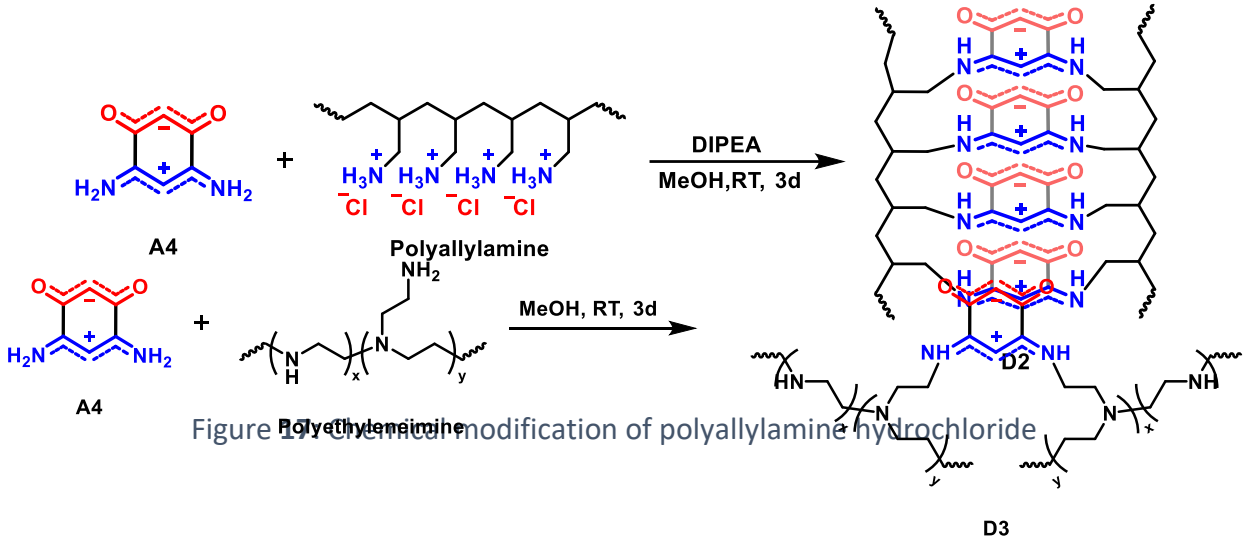


Figure 17: Chemical modification of polyallylamine hydrochloride

Figure **18**: Modification of branched polyethyleneimine

Although we managed to isolate a crosslinked polymer incorporating zwitterionic cores the compound **D2** was completely insoluble in any solvent, reason why the next polymer of our choice was a more soluble one with a lower molecular weight as well namely branched polyethyleneimine (Figure **18**).

Conclusions

The present thesis intitulated “Ground state quinoidal zwitterions as molecular tools for science” had three main milestones divided in some cases in different objectives. First objective on the organic chemistry front is to push further the chemistry of benzoquinonemonoimine zwitterions through the already known transamination reaction which is shown in the **Chapter 3**. Although the transamination reaction was the key path to modify zwitterions the reaction with polyamines was not explored in too much depth. In an attempt to mimic the structure of the cyclam compound **B2** was discovered. Other reactions were performed with polyamines but only the ones containing an odd number of carbons in their chain could form macrocycles through a one pot reaction. The same type of reaction was expected from the reaction with meta phenylenediamine, but the same outcome could not be obtained from a one pot reaction

which lead to the use of difluoro dinitrobenzene to obtain the azacalixarene incorporating a zwitterionic core.

The second objective on the organic chemistry front was to discover a consistent synthesis path similar to the transamination reaction which would allow the introduction of a desired substituent on the central carbon of the oxonol subunit. Several C substituted compounds exist in the current literature but it's not a consistent way. The proposed method described in the **Chapter 4** is a promising alternative for obtaining various C substituted zwitterions. The third and final objective of this milestone of the organic chemistry of the zwitterion is to connect two zwitterionic cores together through a C-C bond which for this particular challenge there are no results obtained.

The second milestone of the thesis is to bridge the two branches of chemistry the organic and polymer chemistry. The work done is presented in the **Chapter 5**. In order to obtain polymers containing the **A4** zwitterions two synthetic paths were approached. Using the zwitterion as a monomeric unit and attempt to polymerize it while maintaining the zwitterionic character or to modify an already formed polymer with **A4** zwitterion. The latter approach proved more successful, but the first approach is still feasible as long as a more reactive polymerizable group can be introduced.

The third and final milestone is to broaden the applications of the BQMI zwitterions which have been obtained. As described in **Chapter 4** coordination complexes of the classical and C -substituted zwitterions were explored for their potential pyridine sensors. Throughout the research activity applications for the macrocyclic compounds were searched but with no success.

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