ROMANIAN ACADEMY
School of Advanced Studies of the Romanian Academy
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SUMMARY OF DOCTORAL THESIS

PROLIGANDS AND COORDINATION COMPOUNDS HAVING FLEXIBLE AND HYDROPHOBIC MOIETIES, CAPABLE OF SELF-ORGANIZATION

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2023

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I. INTRODUCTION

Research context and novelty

With a history of more than 150 years, organosilicon compound chemistry is still an important research topic nowadays. Among the pioneers of this field are J.F. Hyde and F.S. Kipping who during the 30's–40's discovered the siloxane polymers. Since then, siloxane polymers acknowledged a huge importance and are being encountered in many humankind activities. Organosilicons represent a bridge between the inorganic silicon and organic compounds. Distinct properties that make them special as compared with other molecules are their high conformational flexibility and low surface energy. These features originate from the nature of the Si-C bond and the organic groups (usually methyl) attached to the silicon atoms. Methyl groups hinder the assembly of silicones in well-organized solid structures, making them difficult to be crystallized. While the silicon atom as either silanes or siloxanes is present in many compounds or materials, it is still very rare in metal complexes.

An original idea approached a few years ago in our group was to develop new ligands containing highly flexible and hydrophobic moieties, such as tetramethyldisiloxane, dimethyl/diphenyl silane, or trimethylsilyl (Turcan-Trofin *et. al*., 2018; Vlad *et. al*., 2018; Vlad *et. al*., 2017; Zaltariov *et. al*., 2016; Vlad *et. al*., 2016; Soroceanu *et. al*., 2015a; Vlad *et. al*., 2014). Despite their flexibility and hydrophobicity, it was possible to crystallize some of their metal complexes and analyze them through single-crystal X-ray diffraction. Several classes of new ligands and metal complexes containing the above-mentioned moieties were synthesized within our group and they showed interesting self-assembly ability (Turcan-Trofin *et. al*., 2019a; Soroceanu *et. al*., 2015b), catalytic (Zaltariov *et. al*., 2017; Soroceanu *et. al*., 2013a) or magnetic (Shova *et. al*., 2017a; Shova *et. al*., 2017b) properties, as well as biologic activity (Turcan-Trofin *et. al*., 2019b; Zaltariov *et. al*., 2015a; Zaltariov *et. al*., 2015b).

Within this doctoral thesis, it has been proposed the diversification of ligands and coordination compounds, which contain highly flexible and hydrophobic moieties mainly based on silicones. However, by combining hydrophobic segments with organic polar derivatives, the resulting compounds will possess an amphiphilic character and therefore, self-assembly capacity. Herein, we aimed in controlling the physical states of the new compounds both in solution as well as in bulk and studying the induced properties. It should be mentioned that too often the organic or inorganic compounds are studied in solution or solid-state, but the intermediate physical states are ignored. Among the physical states that should be taken into account, is the amorphous phase, as either glassy or viscous states, liquid crystals with multiple mesophases, or polymorphs. Depending on the control of these physical states we attempted in finding their potential applications.

Research objectives

The objectives of this doctoral thesis consisted of:

- The synthesis of ligands containing silicon or alkylic moieties and their structural characterization;
- The complexation of metal ions with the synthesized ligands;
- The study of self-assembly capacity both in solution and in bulk;
- The study of phase transitions-induced properties: optical, magnetical or electrical;
- Approaching the identified properties from the potential application view.

The main results

Six new classes of organic or inorganic compounds containing silicon were synthesized: 1,3-bis(3-aminopropyl)tetramethyldisiloxane-based Schiff bases (**I**) and their metal complexes (**II**), ethers of salicylaldehyde derivatives and their further derivatization (**III**), S-alkylated derivatives of 5-amino-2-mercapto-1,3,4-thiadiazole (**IV**) and their Au(II) complexes (**V**), and their Schiff bases with 3,5-dibromosalicylaldehyde (**VI**). To highlight their peculiarities induced by silicon fragments, alkyl analogues were synthesized as benchmarks. In a new approach for making new ligands, a dicarboxylic acid through 1,3-dipolar cycloaddition (Huisgen) and a new imine having tris(trimethylsiloxy)silane moiety were synthesized.

For the first class of compounds (**I**), it has been shown through spectrophotometric techniques their metal binding capacity (Damoc *et. al.*, 2020). It was found that highly flexible ligands have higher binding capacity as compared with rigid ligands. Moreover, it was identified the possibility of thermodynamic control of chemical reactions through micellization processes. The metal complexes of the first class of ligands (**II**), had liquid crystal behaviour, i.e. nematic mesophase, and exhibited good electric response at external electrical fields as well as aggregation-induced emission (Damoc *et. al.*, 2021). They behaved similarly as lyotropic liquid crystals in solution and showed nematic biaxial mesophase, having an additional orthogonal directional order over the main. Within the third class (**III**) was evidenced one of the biggest silacycles and its reaction pathways through experimental and theoretical studies (Damoc *et. al*., 2022). For the fourth class (**IV**), photophysical processes such as double fluorescence, phosphorescence, and excited-state intermolecular proton transfer triggered by aggregation were found (Damoc *et. al*., 2023). For the fifth and sixth classes (**V**) and (**VI**) only the synthesis procedures and their structural characterization were presented. Nonetheless, preliminary studies indicated their potential as thermal actuators relying on LC property, energy-storage materials, and photoactuators.

The thesis itself has an interdisciplinary character, approaching several fields such as organic or inorganic chemistry, supramolecular and colloid chemistry and spectroscopy, or materials chemistry. Some of these results were not published because of the time and complexities.

III. ORIGINAL CONTRIBUTION

III.1. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane-based Schiff bases

This chapter is committed to the synthesis of new Schiff bases starting from 1,3-bis(3-aminopropyl)tetramethyldisiloxane and several aldehydes, and their comparison with similar Schiff bases derived from aliphatic amines. The new compounds were synthesized through the reaction of 1 equivalent of siloxane diamine and 2 equivalents of the corresponding aldehyde (**Scheme 1**).

Since the alkyl spacers do not possess flexibility as high as siloxanes, **H_2L^7** was crystallized and analyzed through single-crystal X-ray diffraction. As far as can be observed (**Figure 1**), this compound has a linear structure and a *trans* configuration.

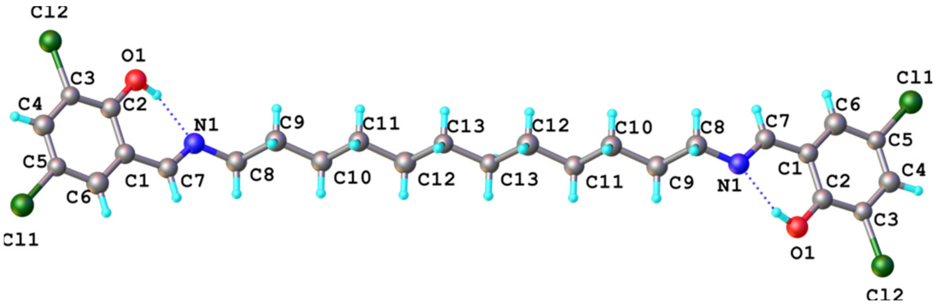
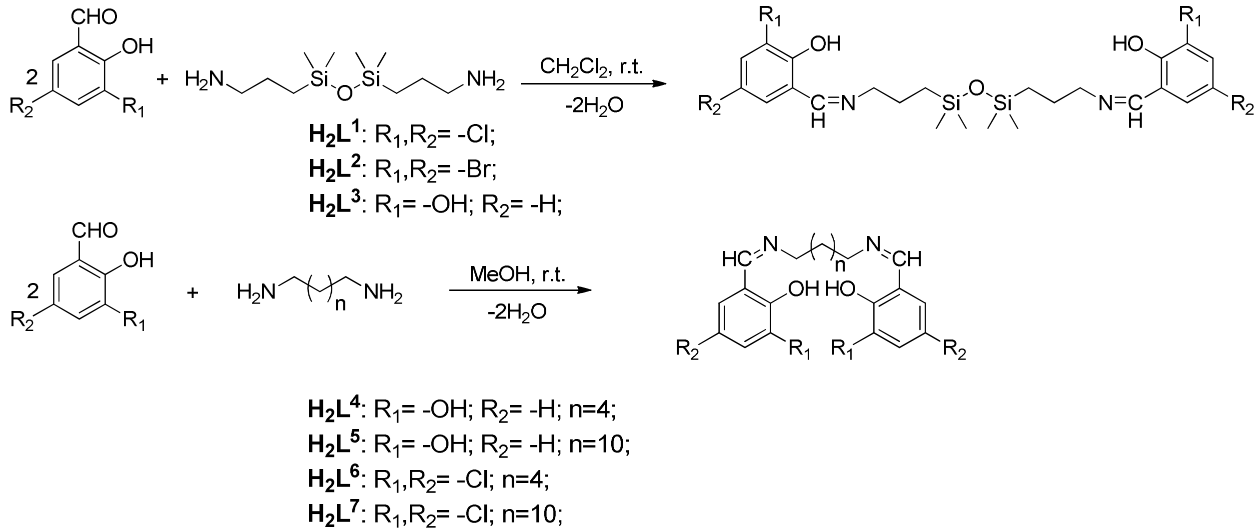


Figure 1. The X-ray diffraction molecular structure of **H_2L^7**. The intramolecular bond length O1-H1···N1 is 2.584 Å.



Scheme 1. The synthesis of new Schiff bases starting from siloxane and aliphatic diamines.

To observe the influence of siloxane fragments over the Schiff bases formation reaction, the rate constants for **H_2L^1**, **H_2L^6**, and **H_2L^7** synthesis were determined. The kinetic measurements have revealed that siloxane diamine lies between hexamethylenediamine and dodecamethylenediamine in terms of reactivity. The highest rate constant was for hexamethylenediamine (5.32×10^{-4} s^{-1}). The lower reactivity of siloxane diamine (2.67×10^{-4} s^{-1}) was assigned to its surface tension (24.93 mN/m), lower than hexamethylenediamine one (35.3 mN/m), which pushed it at the interface air/solvent. To get further information about these processes, another experiment was performed. Using ^1H NMR spectroscopy, the formation reactions of **H_2L^3** and **H_2L^4** were compared with each other. Measurements have revealed a slower reaction of siloxane diamine than the aliphatic one. For the latter the reaction time is fast (1000 min) but with a lower conversion (85 %). For the former, the reaction ended after 2000 minutes, but with a higher conversion (97.6 %). The higher conversion for the siloxane diamine was assigned to the siloxane fragment, which pushed the molecule at the interface, hindering the water access and reaction reversibility. This approach can be *a new way of controlling chemical reactions through micellization processes* (**Figure 2**).

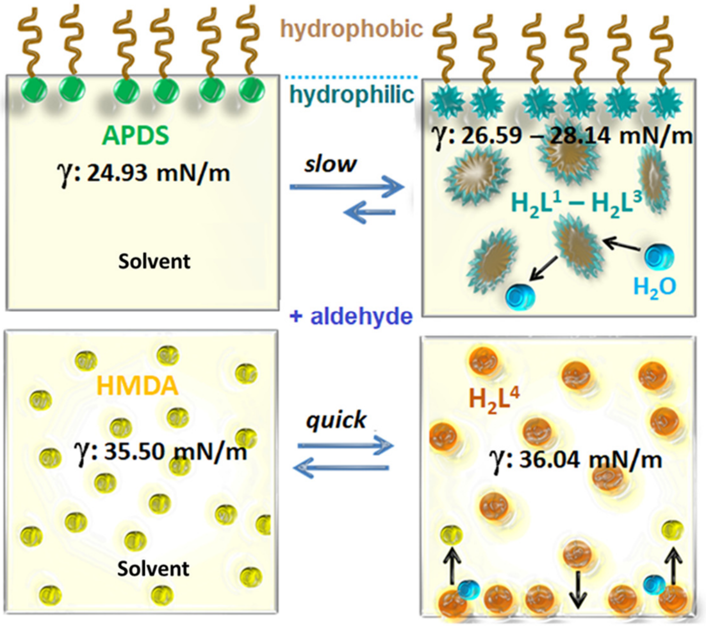


Figure 2. Schematic overview of the thermodynamic control through micellization processes in DMF (γ: 37.1 mN/m). APDS (1,3-bis(3-aminopropy)tetramethyldisiloxane); γ (surface tension); HMDA (hexamethylenediamine).

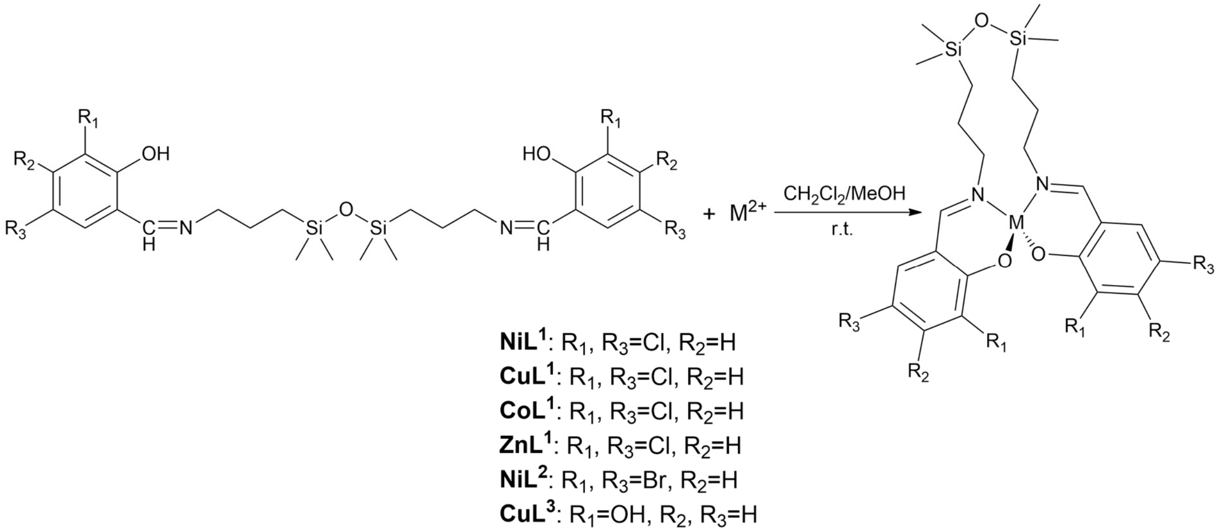
The final goal of this first study was to evaluate the capacity of the new ligands to bind metal ions. Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions were chosen. The complexation reaction was studied in a mixture of methanol-DMF at room temperature for both siloxane- and alkyl-containing Schiff bases. The binding constants vary as follows: **CuL^1 > NiL^1 > ZnL^1 > CoL^1** (**Table 1**). These values obey the Irving and Williams series (Irving și Williams, 1953; Jadhav *et. al*., 2015). The elongation and compression effects, as the Jahn-Teller theory says, affect the donor-acceptor interaction, especially in the case of Cu^{2+} (Pui și Cozma, 2003). Similarly, the length and flexibility of ligands may be among the key factors. In the dimethyldisiloxane unit, the rotational energy barrier of the Si-O-Si bond is close to 0 kJ/mol. Therefore, the complexation of metal ions with ligands containing the tetramethyldisiloxane moiety allows for easier stabilization of the chelated metal complexes in either the *cis* or *trans* configuration. On the contrary, using alkyl spacers, because their rotational energy barrier is 14 kJ/mol, can lead to difficult stabilization of metal complexes with ligands containing this moiety (Dalia *et. al*., 2018). Hence, as can be concluded from **Table 1**, the binding constants of Schiff bases with alkyl spacers have lower values than those with siloxane spacers.

Table 1. Binding constants (K) determined by the Hildebrand-Benesi method.

Compound	**Log K**
CuL^{1}	4.52
ZnL^{1}	4.42
NiL^{1}	4.47
CoL^{1}	3.88
NiL^{2}	4.37
CuL^{3}	4.47
CuL^{4}	3.75
CuL^{5}	4.34
CuL^{6}	4.34
CuL^{7}	4.40

III.2. Metal complexes of 1,3-bis(3-aminopropyl)tetramethyldisiloxane-based Schiff bases

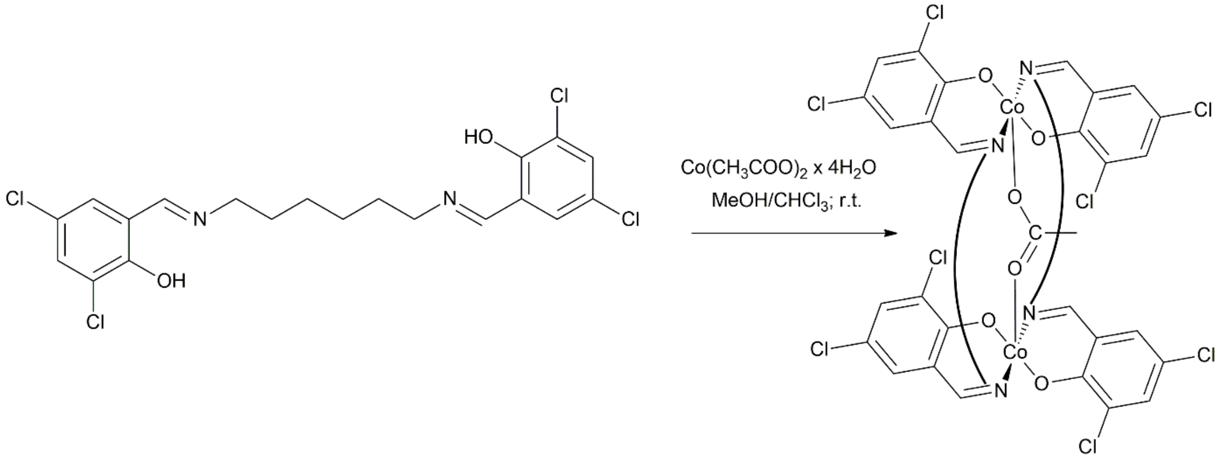
In the following study, coordination compounds of some of the previously presented Schiff bases are approached from a supramolecular point of view. Six new coordination compounds were synthesized by reacting the Schiff bases prepared as above with the corresponding metal ion in a 1:1 ratio (**Scheme 2**).



NiL^{1}: R$_1$, R$_3$=Cl, R$_2$=H
CuL^{1}: R$_1$, R$_3$=Cl, R$_2$=H
CoL^{1}: R$_1$, R$_3$=Cl, R$_2$=H
ZnL^{1}: R$_1$, R$_3$=Cl, R$_2$=H
NiL^{2}: R$_1$, R$_3$=Br, R$_2$=H
CuL^{3}: R$_1$=OH, R$_2$, R$_3$=H

Scheme 2. Representation of the reactions leading to the new coordination compounds.

To compare the properties of **CoL^1**, another cobalt complex was synthesized using the ligand from the condensation reaction of 3,5-dichlorosalicylaldehyde with hexamethylenediamine and Co(Ac)$_2$x4H$_2$O (**Scheme 3**). The crystallographic analysis indicates the formation of a dinuclear complex, in which the cobalt ions are interconnected, both by two **L^6** ligand molecules and by a bridging acetate ion, **[µ-acetato-Co$_2$(L^6)$_2$]**. The oxidation state of the metal ions is mixed, respectively Co(II) and Co(III), and the coordination geometry of the cobalt ions is square pyramidal in the *trans* configuration. However, taking into account the poor quality of collected data, a high-resolution X-ray diffraction analysis is needed. DSC analysis has not shown any phase transition for **[µ-acetato-Co$_2$(L^6)$_2$]** in the studied temperature range, -150 - +200 ºC. (**Figure 3a**). The endothermal peak at 79 ºC is associated with solvent losses (-1.28 %), in agreement with thermogravimetric analysis. This information was strengthened by POM analysis, where any phase transition has not been observed.



Scheme 3. Synthesis of the reference cobalt complex and its molecular structure based on the collected data (square brackets represent the hexylene moiety).

Instead, the **CoL^1** complex shows multiple phase transitions: glass transition at room temperature, mesomorphic features above 110 ºC, and izotropization 201 ºC (**Figures 3b–g**). It can be concluded that using tetramethyldisiloxane moiety is a straightforward approach for bulk self-assembly. Even if the phase transition temperature to liquid crystals is high, these are stable at room temperature for days.

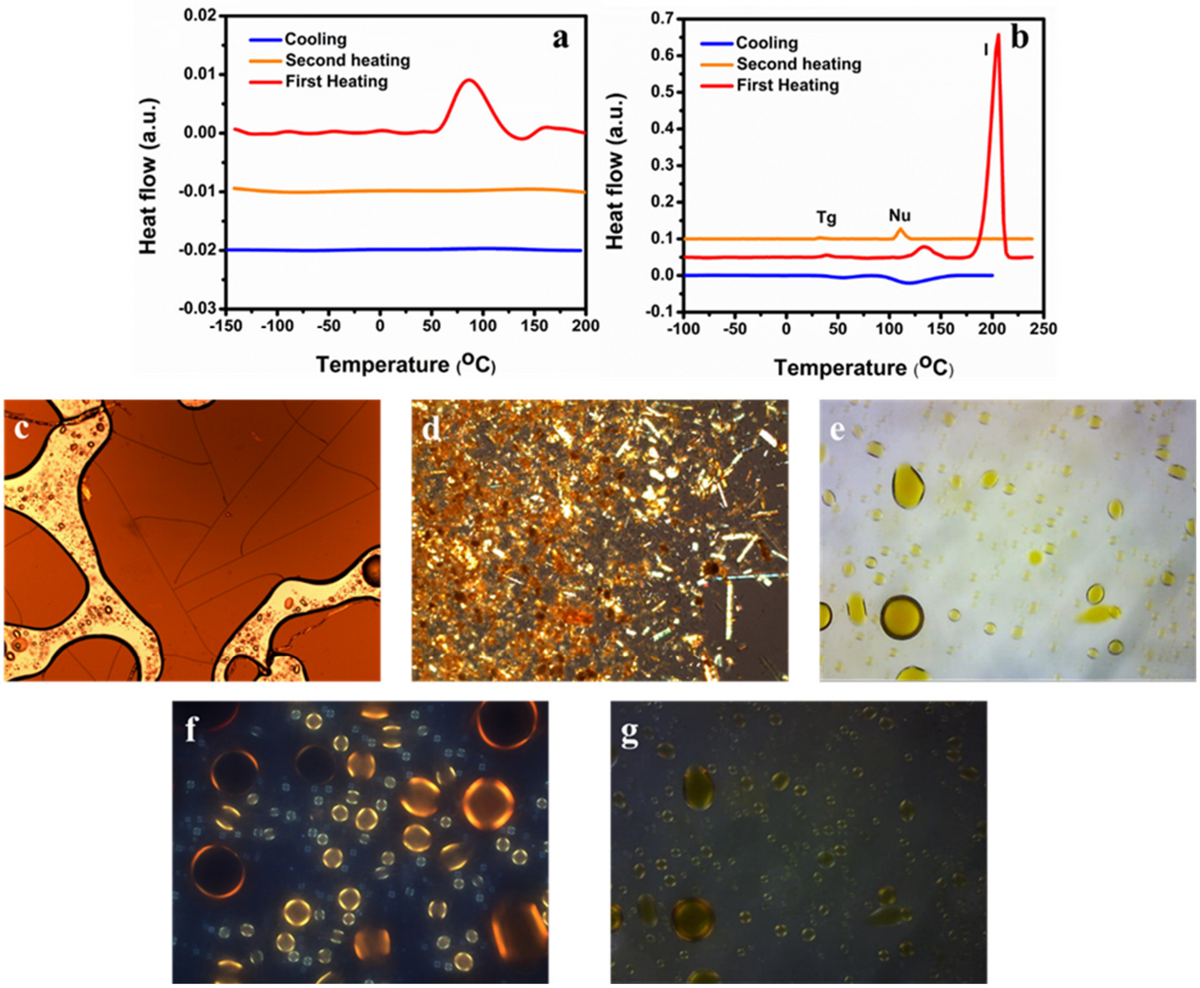
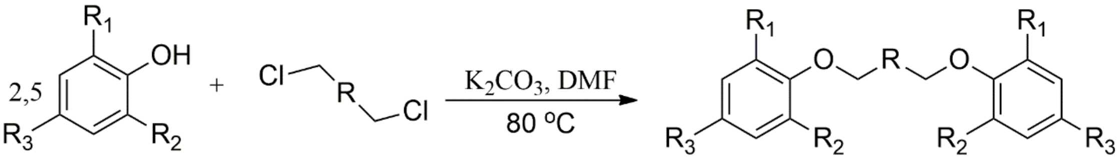


Figure 3. DSC curve for **[μ-acetato-$Co_2(L^6)_2$]** (a); DSC curve for **CoL^1** (b); POM images of **CoL^1** complex in different physical states: glassy state at room temperature, 10x (c); crystalline powder at room temperature, 10x (d); nematic LCs seen with aligned polarizers at 150 °C, 10x (e); dark field at 150 °C, 50x (f); and cross polarizers at 150 °C, 10x (g).

III.3. Silicone derivatives etherification

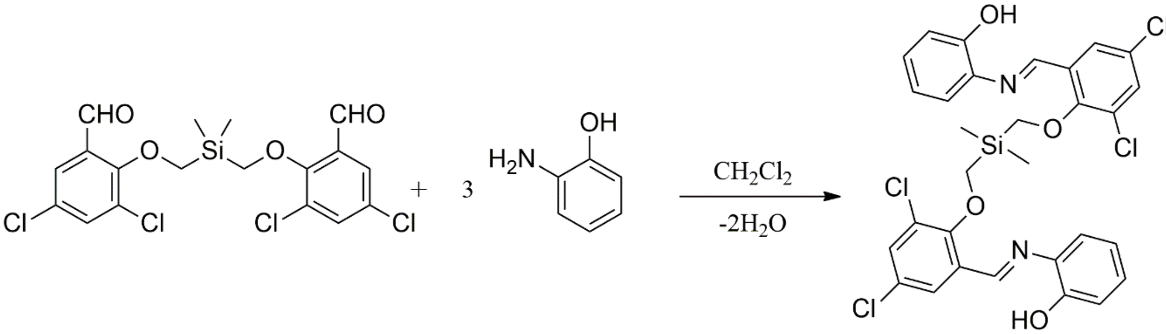
To enlarge the range of ligands containing silicon in their structure with metal ions binding ability, especially Pt^{2+}, new aldehydes were designed to be reacted with amines when obtaining imines. While the organic synthesis was successful, the complexation reaction with Pt^{2+} did not take place. The Pt^{2+} ions catalyzed these reactions to new unexpected organic structures. One of these structures was a silacycle, which is one of the biggest reported in the literature (Han *et al.*, 2020; Wang *et al.*, 2020; Lips *et al.*, 2014). Starting from 2.5 equivalents of phenolic derivatives and 1 equivalent of silicon halide derivatives, and using K_2CO_3 and DMF, three new ethers were obtained (**Scheme 4**).



L^{12}: R=-Si(CH_3)$_2$-; R_1=-CHO; R_2,R_3=-Cl
L^{13}: R=-Si(CH_3)$_2$-O-Si(CH_3)$_2$-; R_1=-CHO; R_2,R_3=-H
L^{14}: R=-Si(CH_3)$_2$-O-Si(CH_3)$_2$-; R_1,R_2=-H; R_3=-CHO

Scheme 4. Derivatization of silicon-containing compounds through etherification reactions.

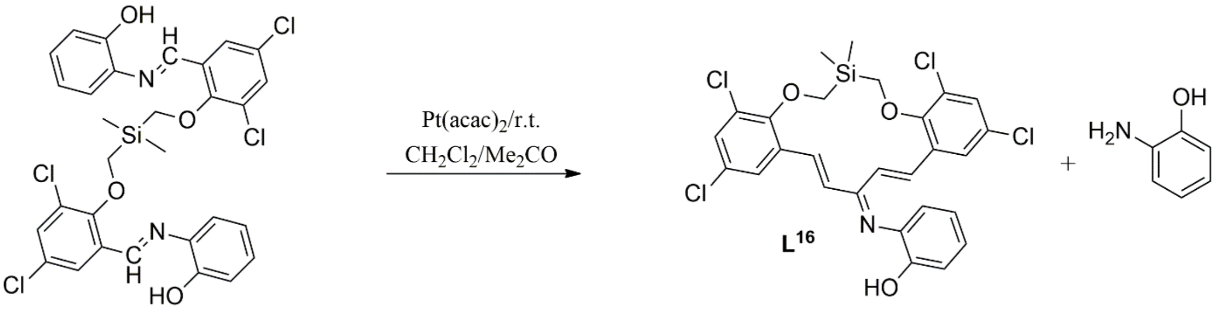
To obtain a new imine with metal ions binding capacity, bis-aldehyde **L**^{12} was reacted with 3 eq. of 2-aminophenol, obtaining bis-imine **L**^{15} (**Scheme 5**).



L^{15}

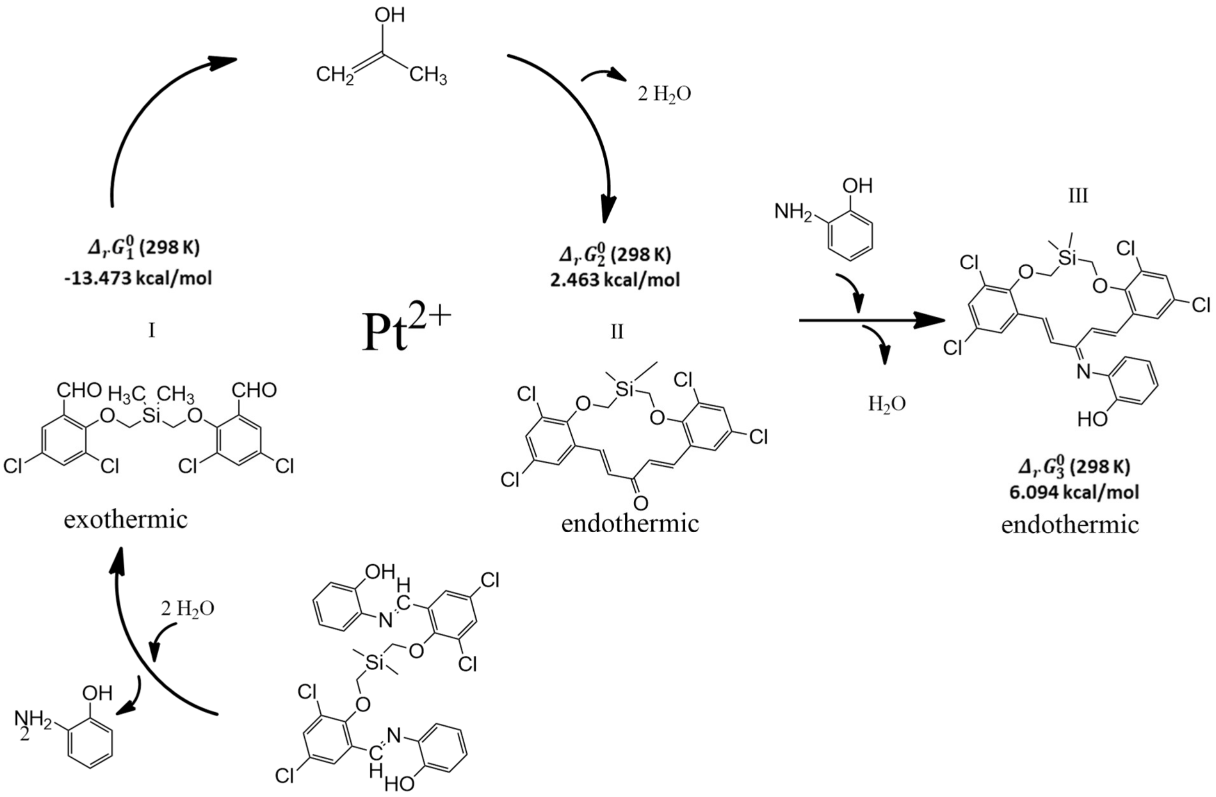
Scheme 5. Bis-aldehyde **L**^{12} reaction with 2-aminophenol leading to the bis-imine **L**^{15}.

Bis-imine **L**^{15} was further reacted with Pt(acac)$_2$, to obtain new Pt(II) complexes. All the analyses indicated a catalytic activity of the Pt(II) salt, leading to a fourteen-membered silacycle (**Scheme 6**).



Scheme 6. The fourteen-membered silacycle **L**^{16} synthesis starting from bis-imine **L**^{15} and Pt(acac)$_2$.

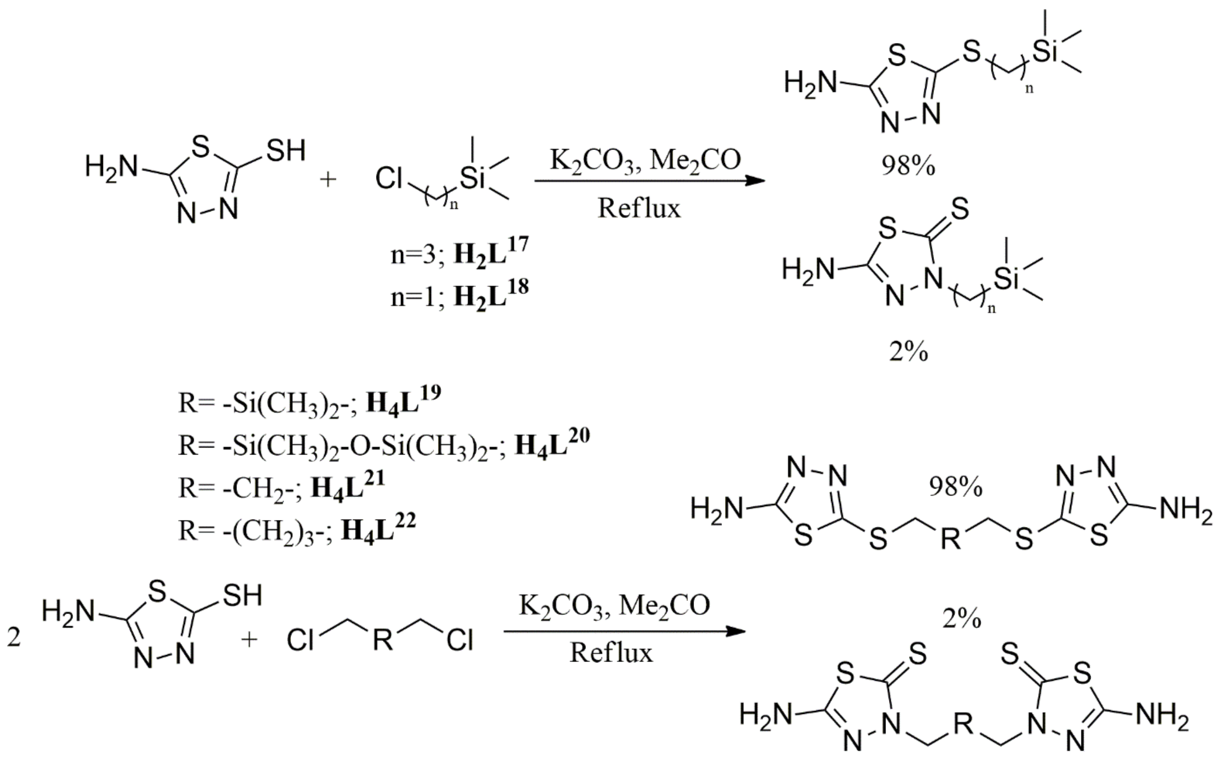
Taking into account all the above-mentioned data, a reaction pathway is proposed (**Scheme 7**). In the first step, an intermediate Pt(II) complex is supposed which undergoes an imine bond cleavage induced by the Pt^{2+} ions and resulting in the bis-aldehyde $\mathbf{L^{12}}$ and two molecules of 2-aminophenol. Looking at the silacycle $\mathbf{L^{16}}$ structure, it can be considered that either acetylacetone or acetone can participate in its reaction. Acetylacetone can participate by methylene active group (Knoevenagel condensation) or by a methyl group (aldol condensation) (Martichonok *et al.*, 2014). Acetone can participate only in aldol condensation as an enol tautomer (Bohre *et al.*, 2015). Performing several experiments, it was found that acetone is involved in the cyclization process through a double aldol condensation. In the third step, the remaining carbonyl group would presumably react with a 2-aminophenol molecule leading to the silacycle $\mathbf{L^{16}}$.



Scheme 7. The proposed reaction pathway to the silacyle $\mathbf{L^{16}}$.

III.4. S-alkylation of silicon derivatives with 5-amino-2-mercapto-1,3,4-thiadiazole

To obtain new performant luminophores, the 5-amino-2-mercapto-1,3,4-thiadiazole was S-alkylated with aliphatic halides containing silane ($\mathbf{H_2L^{17}}$, $\mathbf{H_2L^{18}}$, $\mathbf{H_4L^{19}}$), disiloxane ($\mathbf{H_2L^{20}}$), or hydrocarbons ($\mathbf{H_2L^{21}}$, $\mathbf{H_2L^{22}}$) (**Scheme 8**). Aside from the S-alkylation products, N-alkylation by-products were found in each of the reactions (about 2%) and removed while washing with acetone and petroleum ether. The two classes of weakly conjugated units, namely, permethylated silicon- and hydrocarbon-based compounds, were chosen to compare their optical properties.



Scheme 8. 5-amino-2-mercapto-1,3,4-thiadiazole S-alkylation with aliphatic halides.

In the crystal structure of compounds $\mathbf{H_2L^{17}}$, $\mathbf{H_4L^{20}}$, and $\mathbf{H_4L^{22}}$, intermolecular $N\text{-}H\cdots N$ hydrogen bonds that create a 2D supramolecular architecture were highlighted. On the other hand, the crystal structure of the compound $\mathbf{H_2L^{18}}$ is based on a 1D architecture. A special case is that of the compound $\mathbf{H_4L^{19}}$. The intermolecular interactions in this compound are supplemented by π-π ones between the thiadiazole rings with centroid-centroid distances of 3.772(3) Å, giving rise to a 3D supramolecular structure.

It has been revealed that silicon-containing compounds have twisted supramolecular structures, while hydrocarbon-containing compounds have planar structures. All six S-alkylated aminothiadiazoles have no emission in solution, but only through their aggregation or in the solid state. They have multiple excitation-dependent emissions in Vis and NIR domains and depend on the dispersion medium too (**Figure 4**).

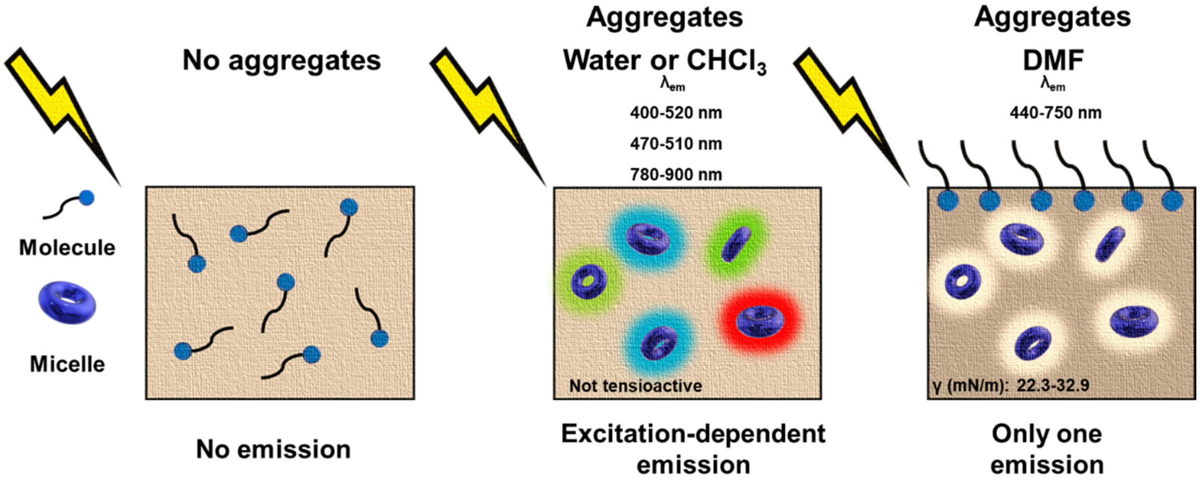


Figure 4. Graphical representation of the aggregation-induced emission. In solid state is the same behaviour as in water or $CHCl_3$.

Time-resolved spectroscopy revealed two fluorescence, both blue and green, and NIR phosphorescence (**Figure 5**). By transient absorption analysis were found high-energy excited state processes, which were associated with pseudo-ESIPT (excited state intermolecular proton transfer), due to the strong intermolecular hydrogen bonding N-H···N. Twisted structures were found to have higher quantum yields than planar structures. The excited-state absorption bands, the excitation-dependent emission lifetimes, the excitation-dependent quantum yield, and the differences between absorption and excitation spectra supported the anti-Kasha proton transfer (i.e., in the high-energy excited states).

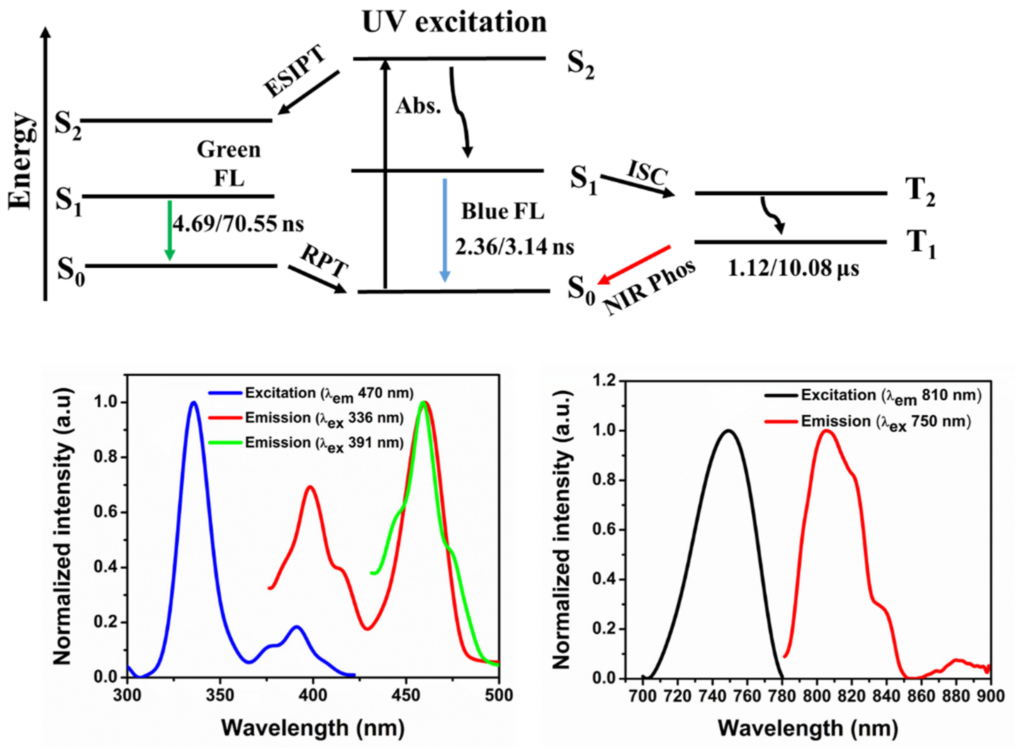
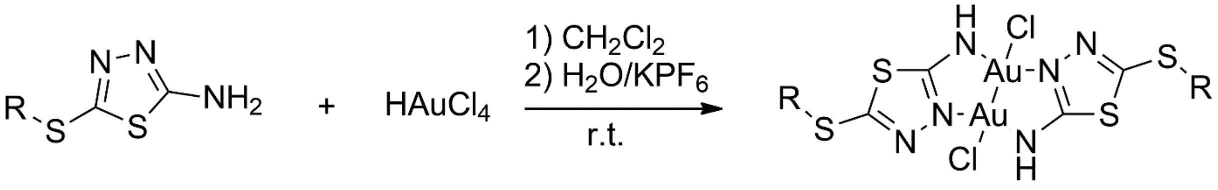


Figure 5. Schematic representation of the proposed emission pathways (up) and solid-state emission spectra (bottom) of S-alkylated aminothiadiazoles.

III.5. Gold (II) complexes of the S-alkylated 5-amino-2-mercapto-1,3,4-thiadiazoles

The next synthetic pathway after the aminothiadiazoles S-alkylation with silicone or aliphatic haloderivatives was the complexation of some metal ions. Since the Au^{n+} ions are thiophilic (Pyykkö, 2004), but also because of their known photophysical properties (Fujisawa *et al.*, 2018; Li *et al.*, 2019), they were selected for the complexation reaction. Three S-alkylated aminothiadiazoles, **H_2L^{17}**, **H_2L^{18}**, and **H_2L^{24}**, were reacted with $HAuCl_4$ when obtaining new dinuclear gold complexes: **$[(HL^{17})_2Au_2Cl_2]$, $[(HL^{18})_2Au_2Cl_2]$**, and **$[(HL^{24})_2Au_2Cl_2]$** (**Scheme 9**).

The three new gold complexes were isolated as red acicular crystals and analyzed by single-crystal X-ray diffraction (**Figure 6**). It can be noticed their similar structures. Each of the Au^{2+} ions has coordination number 4 and square planar geometry. The initial Au^{3+} ions were reduced to Au^{2+}. Unexpectedly, Au^{2+} do not coordinate with the S atom, but with an N atom of the thiadiazole ring, to the -NH_2 group through mono-deprotonation, keeps a Cl atom, and forms a metallic bond with another Au^{2+} ion. The Au-Au bond takes values of 2.5383(5) Å for **[(HL^{17})$_2$$Au_2Cl_2$]**, 2.5344(14) Å for **[(HL^{18})$_2$$Au_2Cl_2$]**, and 2.5293(18) Å for **[(HL^{24})$_2$$Au_2Cl_2$]**, and all structures are in *trans* configuration. Through Au-Au bonds, two five-membered chelate rings are generated.



R= -(CH_2)$_5$-CH_3; [(HL^{24})$_2$$Au_2Cl_2$]
R= -CH_2-Si(CH_3)$_3$; [(HL^{18})$_2$$Au_2Cl_2$]
R= -(CH_2)$_3$-Si(CH_3)$_3$; [(HL^{17})$_2$$Au_2Cl_2$]

Scheme 9. Dinuclear Au(II) complexes synthesis.

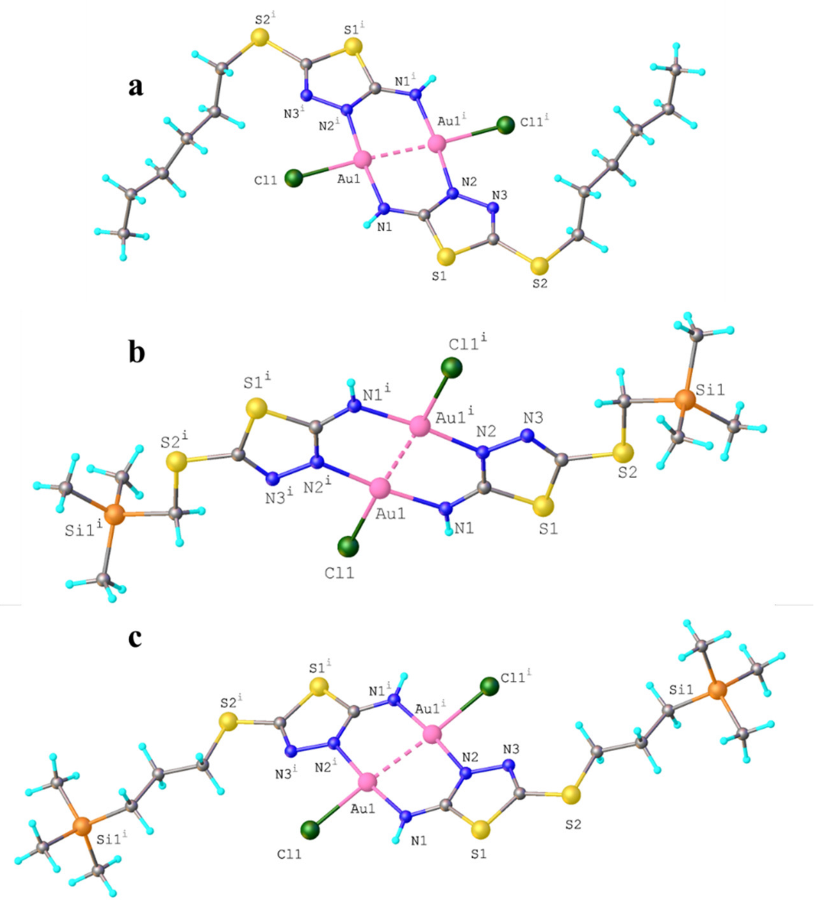
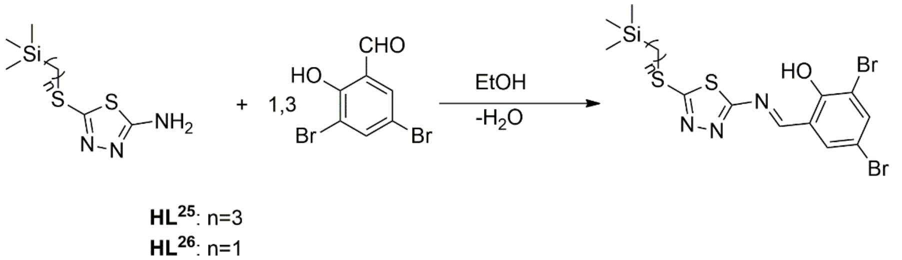


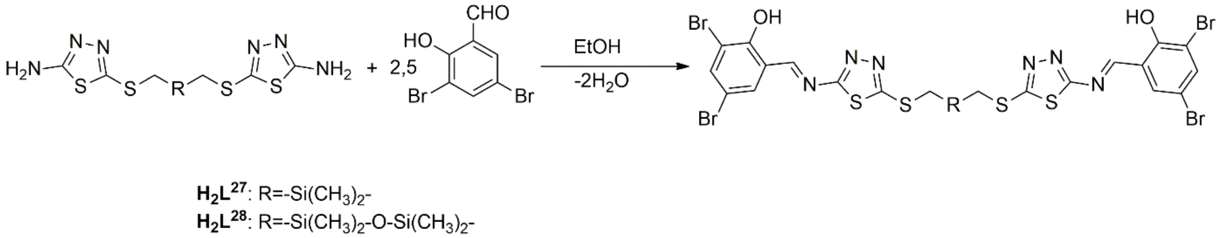
Figure 6. Au(II) complexes molecular structures determined through X-ray diffraction: **[(HL^{24})$_2$$Au_2Cl_2$]** (a); **[($HL^{18}$)$_2$$Au_2Cl_2$]** (b); and **[($HL^{17}$)$_2$$Au_2Cl_2$]** (c).

III.6. 3,5-Dibromosalicylaldehyde-based Schiff bases with the S-alkylated 5-amino-1,3,4-thiadiazoles

After identifying the LC property for the metal complexes with salen-type ligands, other structures containing silicon moieties were designed to present mesophases. To fulfil this purpose, the S-alkylated aminothiadiazoles, **H_2L^{17}**, **H_2L^{18}**, **H_4L^{19}**, și **H_4L^{20}**, were reacted with 3,5-dibromosalicylaldehyde and obtained four new imines (**Schemes 10−11**): two mono-imines (**HL^{25}** and **HL^{26}**) and two bis-imines (**H_2L^{27}** and **H_2L^{28}**).



Scheme 10. **HL^{25}** and **HL^{26}** synthesis.



Scheme 11. **H_2L^{27}** and **H_2L^{28}** synthesis.

HL^{25} and **HL^{26}** were crystallized and analysed using X-ray diffraction. The particular interest was to evaluate their supramolecular structures and check if there are π-π interactions, of particular interest for inducing improved electrical properties. For **HL^{26}**, π-π interactions take place between an aromatic ring and a thiadiazole ring with centroid-centroid distances of 3.735–3.797 Å (**Figure 7**). For **HL^{25}**, π-π interactions were not identified. However, **HL^{25}** has a chiral helical supramolecular structure (**Figure 8**). Its crystalline structure consisted only of the R enantiomer (right-handed). The helical pitch, which describes the distance between two molecules within the spiral is 5.856(3) Å. This property will be translated to the LC property, as shown below.

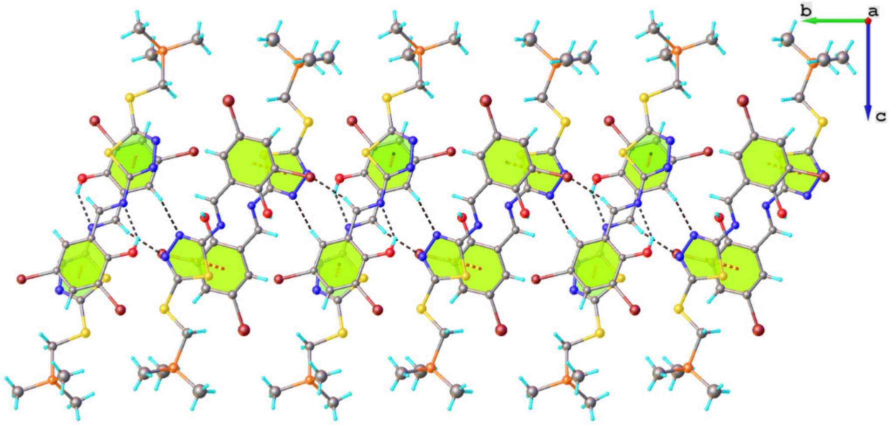


Figure 7. HL^{26} 2D supramolecular structure.

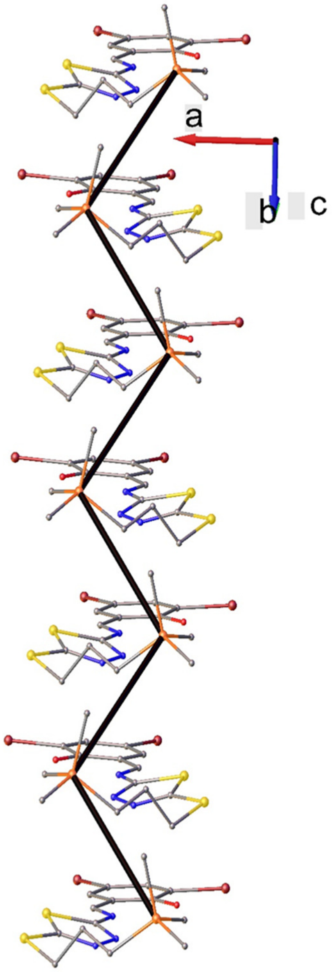


Figure 8. HL^{25} supramolecular chiral structure (R).

Several phase transitions were identified through DSC analysis. All imines have glass transition in the range of 10–30 °C. Within the range of 50–140 °C, each compound has several endothermal phase transitions. The multiple phase transitions were assigned to the LC property and izotropization. The izotropization occurs at 101.2 °C (ΔH,14,45 J/g). On the second heating, nematic columnar LCs appeared at 30 °C, and the phase distribution is homogenous (**Figure 9a**). Around 40 °C, nematic chiral mesophases (**Figures 9b and c**) and smectic phases (**Figure 9d**) appear at the same time, and their distribution is not homogenous. Nematic droplets appeared at 85 °C (ΔH,-4.48 J/g), regardless of the heating or cooling cycle (**Figures 9e and f**).

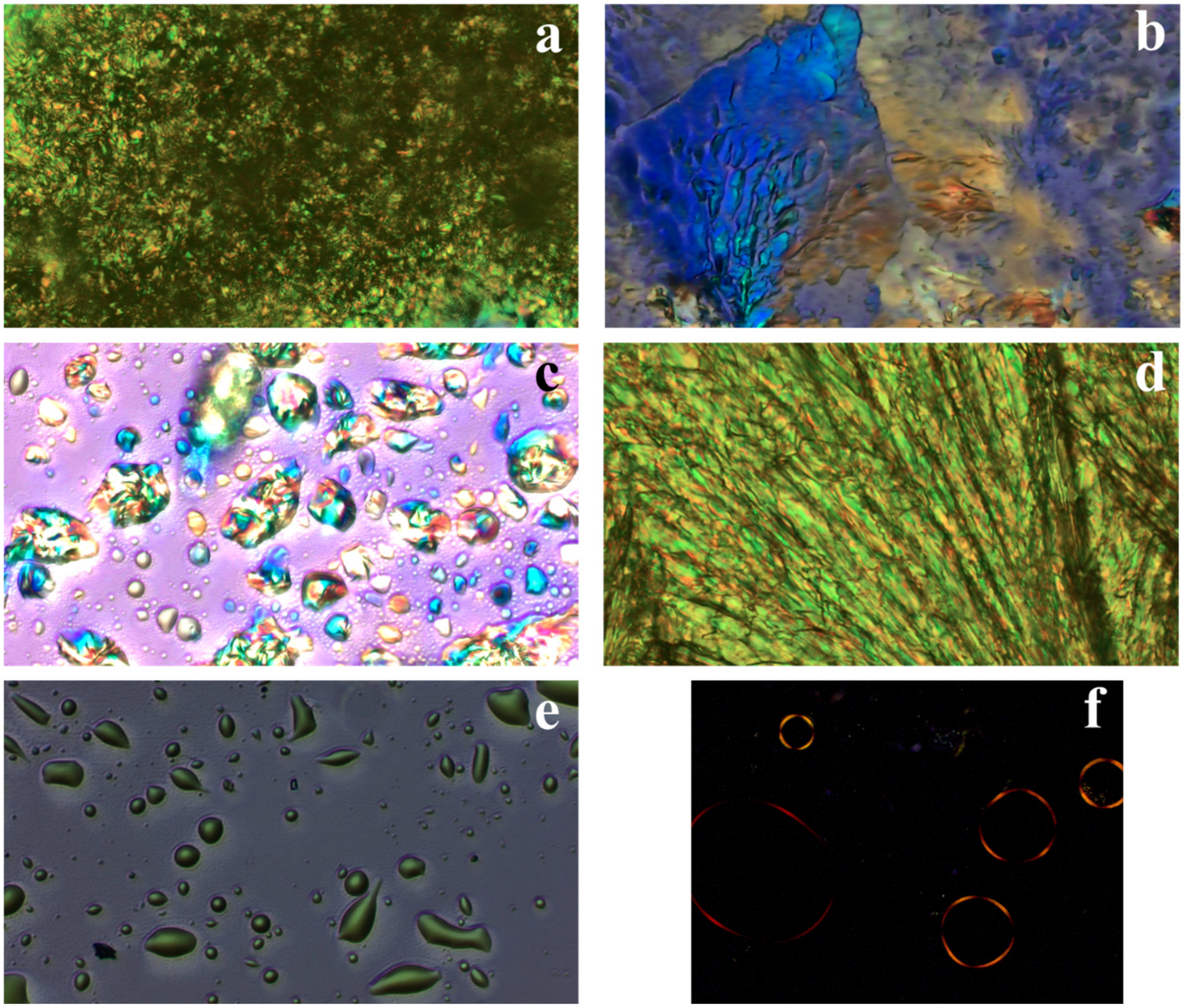
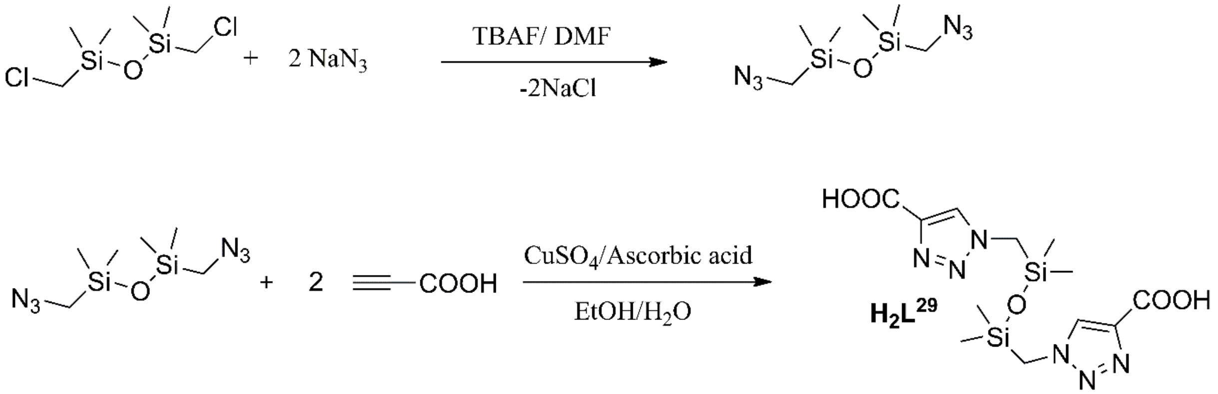


Figure 9. HL^{26} LCs seen by optical polarized microscopy: nematic columnar at 30 °C (a); nematic chiral at 40 °C (b); nematic chiral droplets at 40 °C (c); smectic mesophase at 40 °C (d); nematic droplets seen with aligned polarizers (e) and dark field (f) at 85 °C. Images are recorded with a resolution of 0.02 mm.

III.7. New silicon derivatives bearing organic moieties

To obtain a new dicarboxylic acid, the 1,3-bis(chloromethyl)tetramethyldisiloxane was reacted with NaN_3 in DMF and using tetrabutylammonium fluoride as a phase transfer reagent, when obtaining a bis-azide. The latter was isolated and further reacted with propiolic acid using a Cu(I) catalyst generated *in situ* by the reduction of anhydrous $CuSO_4$ with ascorbic acid (Rostovtsev *et al.*, 2002). This procedure afforded the dicarboxylic acid **H_2L^{29}** (**Scheme 12**).



Scheme 12. H_2L^{29} synthesis through 1,3-dipolar Huisgen cycloaddition.

An interesting particularity is the Si-O-Si valence angle of 180° (**Figure 10**). This is rarely seen for the siloxane compounds (Glidewell şi Liles, 1976), the most usual value being around 145°. A value of 180° of the angle would suggest a 100% contribution of the π component in the Si-O bond. However, the Si-O length value is 1.6102(1) Å, very slightly modified than in other compounds, which does not support the aforementioned hypothesis.

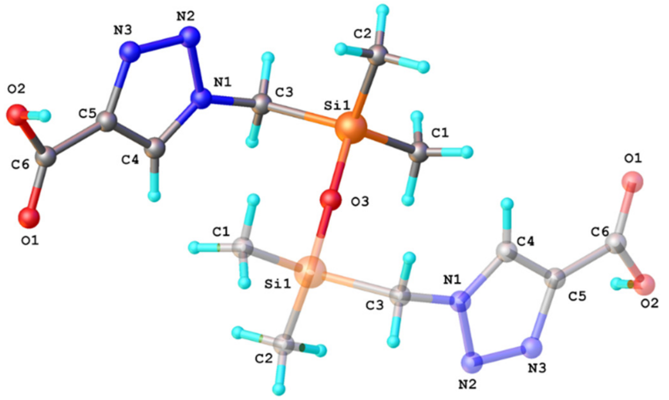
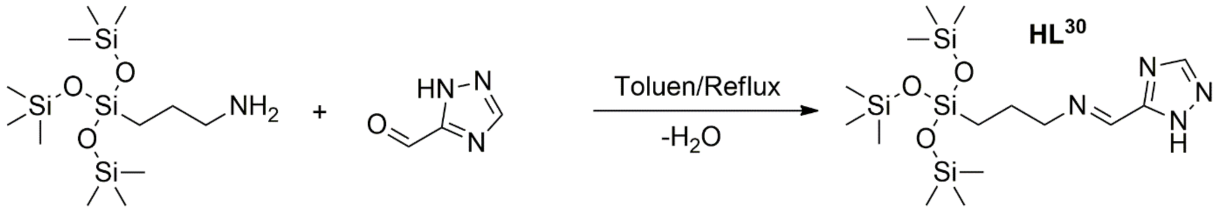


Figure 10. The molecular structure of **HL^{29}** determined through single-crystal X-ray diffraction.

The next synthesized silicon derivative was a tris(trimethylsiloxy)silane. By reacting the 3-aminopropyltris(trimethylsiloxy)silane with a 1,2,4-triazole having a free formyl group, the imine **HL^{30}** was obtained (**Scheme 13**).



Scheme 13. HL^{30} synthesis.

IV. GENERAL CONCLUSIONS

A series of organosilicon compounds, which contain functional groups with metal ions binding capacity were developed and for some of them were isolated the corresponding coordination compounds. The compounds, consisting of ligands and coordination compounds, are originally by the nature of chemically associated structural fragments, one of which is always a unit containing silicon (silane or disiloxane), which is the central core of the doctoral thesis. Known to be highly flexible and hydrophobic, these moieties are physically incompatible with any other organic or inorganic structures and by their chemical coupling provide several unique peculiarities to the new compounds. Instead, a major drawback is the limitation of new compounds to crystallize creating a huge challenge in their isolation and characterization.

Experimental procedures were developed for isolating these classes of compounds in the crystalline state and analysing them by X-ray diffraction. Several of their properties (thermal, optical, electrical, magnetical) were studied in a strict relationship with their self-assembly ability in solution or bulk, and for some of them, the potential applications were identified.

The personal contributions are:

1. The synthesis of new organosilicon compounds and their metal complexes

Using 7 commercially silicon-based compounds, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 1,3-bis(2-aminoethylaminomethyl)tetramethyldisiloxane, 1,3-bis(chloromethyl)tetramethyldisiloxane, bis(chloromethyl)dimethylsilane, (3-chloropropyl)trimethylsilane, chloromethyltrimethylsilane, 3-aminopropyltris(trimethylsiloxy)silane, the following new ligands and coordination compounds were designed:

- **7** salen-type Schiff bases having tetramethyldisiloxane spacer;
- **9** coordination compounds;
- a fourteen-membered silacycle, one of the biggest reported;
- a dicarboxylic acid with siloxane spacer having a Si-O-Si valence angle of 180 ^{o};
- a silanol molecule through photocleavage of the Si-O-Si bond;
- an imine having a tris(trimethylsiloxy)silane tail;
- **3** dinuclear Au(II) complexes;
- recording **22** new compounds in the crystallographic databases, CCDC.

2. Highlighting particularities of both synthesis procedures and the resulting compounds

The chemical coupling of highly flexible and hydrophobic silicon-containing moieties with polar organic molecules resulted in:

- thermodynamic control of chemical reactions;
- amphiphilic character due to the polarity difference between the two segments;
- self-assembly capacity in solution (from micelles to lyotropic liquid crystals);
- glass transition temperature and amorphous-crystalline duality;
- liquid crystal behaviour with multiple mesophases.

Most of these particularities were evidenced by comparison with benchmark compounds.

3. Finding new properties for potential applications

- aggregation induced-emission (micelles, liquid crystals, crystals);
- controlling the physical states by using external stimuli, such as magnetic ones;
- controlling magnetic properties through the compounds' physical state (e.g., paramagnetic in the crystalline state and superparamagnetic within nematic mesophase);
- controlling dielectric properties through the compounds' physical state (higher dielectric permittivity within the amorphous state or liquid crystal than crystalline state).

While some of the results corresponded to the initial aim, others generated new ideas being exciting platforms for new research. Some of the presented results were disseminated within the scientific community being the subject of 4 articles and 5 communications, and others will be published soon.

RESULTS DISSEMINATION AND OTHER SCIENTIFIC ACTIVITIES

The presented results within this doctoral thesis were the subject of 4 articles, 5 communications, and 2 posters:

Published articles

1. Damoc, M.; Stoica, A. C.; Macsim, A. M.; Dascalu, M.; Zaltariov, M. F.; Cazacu, M. Salen-Type Schiff Bases Spaced by the Highly Flexible and Hydrophobic Tetramethyldisiloxane Motif. Some Synthetic, Structural and Behavioral Particularities. *J. Mol. Liq.* **2020**, *316*, 113852.
2. Damoc, M.; Stoica, A. C.; Dascalu, M.; Asandulesa, M.; Shova, S.; Cazacu, M. Dual Crystalline-Amorphous Salen-Metal Complexes Behave like Nematic Droplets with AIEgens Vistas. *Dalton Trans.* **2021**, *50* (39), 13841–13858.
3. Damoc, M., Stoica, A.C., Blaj, D.A., Macsim, A.M., Dascalu, M., Cojocaru, C., Shova, S., Cazacu, M. Fourteen-member silacycle built by cascade reactions induced by a platinum catalyst. *J. Mol. Struct.* **2022**, *1269*, 133760.
4. Damoc, M., Tigoianu, R.I., Stoica, A.C., Macsim, A.M., Dascalu, M., Shova, S., Cazacu, M., Micellization Turned on Dual Fluorescence and Room Temperature Phosphorescence by Pseudo-ESIPT in Thiadiazole Derivatives. *J. Phys. Chem . C* **2023**, *127* (1), 99-109.

Communications at scientific events

1. Dual Crystalline-Amorphous Schiff Base Complexes with Unusual Mesogen Phase Behavior (Damoc, M.; Dascalu, M.; Asandulesa, M.; Cazacu, M.); *Scientific Communications Session of Young Researchers*, 19 November, **2020**, Iași, România.
2. Siloxane/Silane Derivatives and Their Gold Complexes: Interfacial Phenomena Based on Photoluminescence (Damoc, M.; Stoica, A.-C.; Dascalu, M.; Macsim, A.M.; Tigoianu, R.I.; Blaj, D.; Rusu, A.G.; Iacob, M.; Cazacu, M.) *Progress in Organic and Macromolecular Compounds Conference MacroIasi'2021,* October 7-9, **2021**, Iași, România.
3. Multi-Step Procedure Leading to a Heterocycle Containing Dimethylsilane Unit (Damoc, M.; Stoica, A.-C.; Blaj, D.; Macsim, A.M.; Dascalu, M.; Cazacu, M.) *Scientific Communications of Young Researchers Macroyouth',* 19 November, **2021**, Iași, România.

4. Efficient Light Harvesting Strategies by Suppressing the Kasha's Rule in Thiadiazole Derivatives (Damoc, M.; Tigoianu, R.I.; Stoica, A.-C.; Macsim, A.M.; Dascalu, M.; Shova, S.; Cazacu, M.), *A XXXVI-a Conferința Națională de Chimie*, Călimăneşti – Căciulata, 4-7 October, **2022**, Vâlcea, România.
5. Merging Hydrophobic Moieties Within Five-Membered Heterocycles. Mighty Approaches Toward Achieving Some Spectacular Phenomena (Damoc, M.; Stoica, A.-C.; Cazacu, M.), *Scientific Communications of Young Researchers Macroyouth*, November 18, **2022**, Iași, România.

Poster presentations

1. Engineering Organic Heterocycles and Silacycles Through a Pt(II) Catalyst (Damoc, M.; Stoica, A.-C.; Cazacu, M.), *The International School on Innovations in Homogeneous and Supported Homogeneous Catalysis*, 25-28 Aprilie, **2023**, București, România.
2. High-Energy Intermolecular Proton Transfer Generating Multiple Emissions in Aminothiadiazole Derivatives (Damoc, M.; Tigoianu, R.I.; Stoica, A.-C.; Cazacu, M.), *Thematic School Vibrational and Electronic spectroscopies applied to the study of reaction mechanisms – MECAREACT*, 18-23 june, **2023**, Paris, France.

Related articles published through collaborations

1. Racles, C.; Zaltariov, M. F.; Damoc, M.; Macsim, A. M.; Iacob, M.; Sacarescu, L. Three Reactions, One Catalyst: A Multi-Purpose Platinum(IV) Complex and Its Silica-Supported Homologue for Environmentally Friendly Processes. *Appl. Organomet. Chem.* **2020**, *34* (3), 1–15.
2. Shova, S.; Vlad, A.; Damoc, M.; Tiron, V.; Dascalu, M.; Novitchi, G.; Ursu, C.; Cazacu, M. Nanoscale Coordination Polymer of Dimanganese(II) as Infinite, Flexible Nanosheets with Photo-Switchable Morphology. *Eur. J. Inorg. Chem.* **2020**, *2020* (21), 2043–2054.
3. Shova, S.; Tiron, V.; Vlad, A.; Novitchi, G.; Dumitrescu, D. G.; Damoc, M.; Zaltariov, M. F.; Cazacu, M. Permethylated Dinuclear Mn(III) Coordination Nanostructure with Stripe-Ordered Magnetic Domains. *Appl. Organomet. Chem.* **2020**, *34* (12), 1–11.
4. Stoica, A. C.; Damoc, M.; Zaltariov, M. F.; Racles, C.; Cazacu, M. Two-Dimensional Coordination Polymers Containing Permethylated Motifs - Promising Candidates for 2D

Emerging Materials. Structural, Behavioral and Functional Particularities. *React. Funct. Polym.* **2021**, *168*, 105039.

5. Stoica, A. C.; Damoc, M.; Tiron, V.; Dascalu, M.; Coroaba, A.; Shova, S.; Cazacu, M., Silanol-functionalized tetranuclear copper complex and its nanoscale-heterogenization by immobilization on glass surface from solution. *J. Mol. Liq.* **2021**, *344*(2-3), 117742.

6. Stoica, A. C.; Damoc, M.; Baltag, L.; Macsim, A. M.; Nicolescu, A.; Dinu, M.V.; Ionita, G.; Cazacu, M., One pot reduction hydrophobization of heterogenized platinum with 1,1,3,3-tetramethyldisiloxane. *Appl. Organomet. Chem.* **2021**, *36*(1), 6485.

7. Ciubotaru, B.I., Dascalu, M., Zaltariov, M.F., Macsim, A.M., Damoc, M., Bele, A., Tugui, C., Varganici, C.D., Cazacu, M., Catalyst-free crosslinked sustainable functional silicones by supramolecular interactions. *React Funct Polym.* **2022**, *181*, 105419.

8. Stoica, A.C., Damoc, M., Cojocaru, C., Nicolescu, A., Shova, S., Dascalu, M., Cazacu, M., Some Theoretical and Experimental Evidence for Particularities of the Siloxane Bond. *Molecules* **2022**, *27*, 8563.

9. Stoica, A.C.; Damoc, M.; Shova, S.; Novitchi, G.; Dascalu, M.; Cazacu, M.A Manganese(II) 3D Metal–Organic Framework with Siloxane-Spaced Dicarboxylic Ligand: Synthesis, Structure, and Properties. *Inorganics* **2023**, *11*, 21.

10. Farcas, A; Damoc, M.; Asandulesa, M.; Aubert, P.H.; Tigoianu, R.I.; Ursu, L.E. The straightforward approach of tuning the photoluminescence and electrical properties of encapsulated PEDOT end-capped by pyrene. *J. Mol. Liq.* **2023**, *376*, 121461.

Research stages

1. **8 December 2019 - 7 January 2020** – research stage at the Institute of Organic Synthesis from National University Taras Shevchenko of Ukraine, Kyiv.
2. **28 August 2021 - 27 September 2021** - research stage at the Institute of Organic Synthesis from National University Taras Shevchenko of Ukraine, Kyiv.

Thematic schools attendance

1. The International School on Innovations in Homogeneous and Supported Homogeneous Catalysis, 25-28 April **2023**, București, România.
2. Thematic School Vibrational and Electronic spectroscopies applied to the study of reaction mechanisms – MECAREACT, 18-23 June **2023**, Paris, France.

Team member in research projects

1. “Recovery of platinum-group metals from spent automotive catalysts using chemical methods” **ECOTECH-GMP,** Contract 76PCCDI/2018 (**2018–2020**).
2. “Emerging 2D materials based on two-dimensional permethylated metal-organic networks” **PerMONSil,** Proiect PN-III-P4-ID-PCE-2020-2000, Contract 207/2021 (**2021–2023**).

Awards

1. ACS Best Presentation Award for the Presentation of Siloxane/Silane Derivatives and Their Gold Complexes: Interfacial Phenomena Based On Photoluminescence. *Progress in Organic and Macromolecular Compounds Conference MacroIasi'2021,* October 7-9, **2021**, Iași, România.

ACKNOWLEDGEMENTS

- To Dr. **Maria Cazacu** for guidance, unlimited support, and advice without whom I could not have finished this PhD thesis;
- To the **Evaluation Committee**, **Acad. Prof. Marius Andruh**, **Prof. Dr. Ing. Nicolae Hurduc**, and **Dr. Carmen Racleş**, for evaluation and approval of the thesis's public defence;
- To the **Guidance Committee** for discussions, advice, and evaluation of the preliminary results;
- To all my colleagues from the **Inorganic Polymers Department** for their support, encouragement, and advice;
- To Dr. **Sergiu Shova** and Dr. **Mirela Zaltariov** regarding the organic and inorganic chemistry discussions;
- To Dr. **Mihaela Dascălu** and Drd. **Alexandru-Constantin Stoica** for single-crystal X-ray diffraction analyses;
- To Dr. **Ana-Maria Macsim** and Dr. **Alina Nicolescu** for NMR analyses;
- To Drd. **Diana Andreea Blaj** and Dr. **Mihaela Silion** for MS analyses;
- To Dr. **Radu Ionuț Tigoianu** for spectroscopic analyses;
- To Dr. **Mihai Asăndulesa** for dielectric spectroscopy analyses;
- To Dr. **Liviu Săcărăscu** for TEM analyses;
- To Dr. **Alina Rusu** for DLS analyses;
- To Dr. **Cristian Dragoș Varganici** for DSC and TGA analyses;
- To Dr. **Corneliu Cojocaru** for DFT theoretical analyses;
- To Dr. **Vasile Tiron** for MFM analyses;
- To Dr. **Codrin Țugui** for 3D printing;
- To Dr. **Bogdan-Constantin Condurache** for VSM analyses;
- To Dr. **Gheorghe Roman** for the synthesis of 4-(((4-chlorophenyl)thio)methyl)-2-hydroxy-benzaldehyde;
- To Dr. **Andrei Dascălu** for PXRD analyses;
- To Dr. **Violeta Melinte** and Dr. **Andrei Bejan** for POM analyses;
- To Dr. **Florica Doroftei** for SEM analyses;
- To Dr. **Aurica Farcaș** for collaboration, discussions, and advice;

- To all my colleagues from the **„Petru Poni" Institute of Macromolecular Chemistry from Iași** for collaborations, discussions, and disponibility;
- To the **"Alexandru Ioan Cuza" University from Iași** and to **Chemistry Faculty Professors** for my initiation within the chemistry field;
- To the **University from Viena, Austria** and to **Prof. Vladimir Arion's group** for elemental analyses;
- To the **Organic Synthesis Institute NAS from Kyiv, Ukraine,** for the synthesis of 1H-1,2,4-triazoles-5-formyl-3-substituted;
- To the **Romanian Ministry of Research, Innovation, and Digitization for financing the projects PN-III-P1-1.2-PCCDI-2017-0185/76PCCDI/2018, PNCDI III, PN-III-P4-ID-PCE-2020-2000**, and **PNCDI III, Contract 207/2021 (2D-PerMONSil)**, projects on which I was a team member.

I want to thank all the professors/mentors/colleagues/friends above-mentioned for contributing to my scientific and personal development and mention I am just one of the authors and this doctoral thesis is teamwork. ***Nihil sine amicis!***

BIBLIOGRAPHY

(1) Bohre, A. *et al.* (2015) ‘Upgrading Furfurals to Drop-in Biofuels: An Overview’, *ACS Sustainable Chemistry and Engineering*, 3(7), pp. 1263–1277. doi: 10.1021/acssuschemeng.5b00271.

(2) Dalia, S. *et al.* (2018) ‘A short review on chemistry of Schiff base metal complexes and their catalytic application’, *International Journal of Chemical Studies*, 6(3), pp. 2859–2866.

(3) Damoc, M. *et al.* (2020) ‘Salen-type Schiff bases spaced by the highly flexible and hydrophobic tetramethyldisiloxane motif. Some synthetic, structural and behavioral particularities’, *Journal of Molecular Liquids*, 316, pp. 113852. doi: 10.1016/j.molliq.2020.113852.

(4) Damoc, M. *et al.* (2021) ‘Dual crystalline-amorphous salen-metal complexes behave like nematic droplets with AIEgens vistas’, *Dalton Transactions*, 50(39), pp. 13841–13858. doi: 10.1039/d1dt01980e.

(5) Damoc, M. *et al.* (2022) ‘Fourteen-member silacycle built by cascade reactions induced by a platinum catalyst’, *Journal of Molecular Structure*, 1269, pp. 133760. doi: 10.1016/j.molstruc.2022.133760.

(6) Damoc, M. *et al.* (2023) ‘Micellization Turned on Dual Fluorescence and Room Temperature Phosphorescence by Pseudo-ESIPT in Thiadiazole Derivatives’, *The Journal of Physical Chemistry C* , 127(1), pp. 99-109. doi: 10.1021/acs.jpcc.2c07651.

(7) Fujisawa, K. *et al.* (2018) ‘Photoluminescence behavior of liquid-crystalline gold(I) complexes with a siloxane group controlled by molecular aggregate structures in condensed phases’, *Polymer Journal*, 50(8), pp. 761–769. doi: 10.1038/s41428-018-0060-8.

(8) Glidewell, C. și Liles, D. C. (1978) ‘The Crystal and Molecular Structure of Oxobis [triphenylsilicon (IV)]’, *Acta crystallographica. Section B, Structural science*, 34(1), pp. 124-128. DOI: 10.1107/S0567740878002435.

(9) Han, J. L. *et al.* (2020) ‘Divergent Synthesis of Vinyl-, Benzyl-, and Borylsilanes: Aryl to Alkyl 1,5-Palladium Migration/Coupling Sequences’, *Angewandte Chemie - International Edition*, 59(16), pp. 6555–6560. doi: 10.1002/anie.201914740.

(10) Irving, H. și Williams, R.P.J. (1953) ‘The stability of transition-metal complexes’, *Journal of the Chemical Society*, 637, pp. 3192-3210. 10.1039/JR9530003192.

(11) Jadhav, S. *et al.* (2015) ‘Determination of stability constant of metal ligand equilibria with special reference to Schiff base and transition elements’, *Der Pharmacia Lettre*, 7(12), pp. 316–320.

(12) Li, L. K. *et al.* (2019) 'Strategies towards rational design of gold(iii) complexes for high-performance organic light-emitting devices', *Nature Photonics*, 13(3), pp. 185–191. doi: 10.1038/s41566-018-0332-z.

(13) Lips, F. *et al.* (2014) 'Reactions of alkenes and alkynes with an acyclic silylene and heavier tetrylenes under ambient conditions', *Organometallics*, 33(21), pp. 6253–6258. doi: 10.1021/om500947x.

(14) Martichonok, V. V. *et al.* (2014) 'On regioselectivity of aldol condensation of aromatic aldehydes with borate complex of acetylacetone', *Synthetic Communications*, 44(9), pp. 1245–1250. doi: 10.1080/00397911.2013.850094.

(15) Pui, A. și Cozma, D.G. (2003) *'The Basics of the Chemistry of Coordinative Compounds'*. Matrixrom.

(16) Pyykkö, P. (2004) 'Theoretical chemistry of gold', *Angewandte Chemie - International Edition*, 43(34), pp. 4412–4456. doi: 10.1002/anie.200300624.

(17) Rostovtsev, V. V. *et al.* (2002) 'A stepwise huisgen cycloaddition process: Copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes', *Angewandte Chemie - International Edition*, 41(14), pp. 2596–2599. doi: 10.1002/1521-3773(20020715)41:14<2596::AID-ANIE2596>3.0.CO;2-4.

(18) Shova, S. *et al.* (2017a) 'An iron(iii)-centred ferric wheel Fe⊂{Fe6} with a siloxane-based bis-salicylidene Schiff base', *Dalton Transactions*, 46(6), pp. 1789–1793. doi: 10.1039/c7dt00141j.

(19) Shova, S. *et al.* (2017b) 'A five-coordinate manganese(III) complex of a salen type ligand with a positive axial anisotropy parameter: D', *Dalton Transactions*, 46(35), pp. 11817–11829. doi: 10.1039/c7dt01809f.

(20) Soroceanu, A. *et al.* (2013a) 'Copper(II) complexes with Schiff bases containing a disiloxane unit: Synthesis, structure, bonding features and catalytic activity for aerobic oxidation of benzyl alcohol', *European Journal of Inorganic Chemistry*, 2013(9), pp. 1458–1474. doi: 10.1002/ejic.201201080.

(21) Soroceanu, A. *et al.* (2013b) 'Ni(II) and Zn(II) complexes with a salen-type ligand derived from 1,3-bis(3-aminopropyl)tetramethyldisiloxane', *Revue Roumaine de Chimie*, 58(2–3), pp. 209–216.

(22) Soroceanu, A. *et al.* (2015a) 'A supramolecular structure based on copper complex of 2,3-

pyridinedicarboxylic acid and 1,3-bis(3-aminopropyl)tetramethyldisiloxane chlorohydrate', *Journal of Molecular Structure*, 1083, pp. 88–94. doi: 10.1016/j.molstruc.2014.11.038.

(23) Soroceanu, A. *et al.* (2015b) 'Supramolecular aggregation in organic solvents of discrete copper complexes formed with organosiloxane ligands', *Soft Materials*, 13(2), pp. 93–105. doi: 10.1080/1539445X.2015.1009551.

(24) Turcan-Trofin, G. O. *et al.* (2018) 'Metallo-supramolecular assemblies of dinuclear Zn(II) and Mn(II) secondary building units (SBUs) and a bent silicon dicarboxylate ligand', *Inorganica Chimica Acta*, 483(1), pp. 454–463. doi: 10.1016/j.ica.2018.08.027.

(25) Turcan-Trofin, G. O. *et al.* (2019a) 'Copper(II) complexes with spherical morphology generated in one step by amphiphilic ligands: in situ view of the self-assembling, characterization, catalytic activity', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 580, pp. 2–12. doi: 10.1016/j.colsurfa.2019.123756.

(26) Turcan-Trofin, G. O. *et al.* (2019b) 'Amphiphilic silicone-bridged bis-triazoles as effective, selective metal ligands and biologically active agents in lipophilic environment', *Journal of Molecular Liquids*, 294, 111560. doi: 10.1016/j.molliq.2019.111560.

(27) Vlad, A. *et al.* (2012a) 'A bis(pyrrole) Schiff base containing a flexible siloxane bridge and its Ni II complex', *European Journal of Inorganic Chemistry*, (31), pp. 5078–5084. doi: 10.1002/ejic.201200612.

(28) Vlad, A. *et al.* (2012b) 'Telechelic or side-functionalized diorganosiloxanes with ferrocenylimine groups', *Synthetic Metals*, 161(23–24), pp. 2659–2668. doi: 10.1016/j.synthmet.2011.09.040.

(29) Vlad, A. *et al.* (2014) 'A 2D metal-organic framework based on dizinc coordination units bridged through both flexible and rigid ligands', *Journal of Molecular Structure*, 1060(1), pp. 94–101. doi: 10.1016/j.molstruc.2013.12.029.

(30) Vlad, A. *et al.* (2016) 'New Zn(II) and Cu(II) complexes with in situ generated N2O2 siloxane Schiff base ligands', *Polyhedron*, 115, pp. 76–85. doi: 10.1016/j.poly.2016.04.038.

(31) Vlad, A. *et al.* (2017) 'Synthesis, Structural Characterization and Antimicrobial Activity of a New Bis-Azomethine With Trimethylsilyl Terminal Groups', *Rev. Roum. Chim*, 62(9), pp. 661–667. Available at: http://web.icf.ro/rrch/.

(32) Vlad, A. *et al.* (2018) 'Synthesis, structural characterization and properties of some novel siloxane-based bis-Schiff base copper(II), nickel(II) and manganese(II) complexes',

Polyhedron, 146, pp. 129–135. doi: 10.1016/j.poly.2018.02.029.

(33) Wang, X. B. *et al.* (2020) 'Controllable Si−C Bond Activation Enables Stereocontrol in the Palladium-Catalyzed [4+2] Annulation of Cyclopropenes with Benzosilacyclobutanes', *Angewandte Chemie - International Edition*, 59(2), pp. 790–797. doi: 10.1002/anie.201913060.

(34) Zaltariov, M. F. *et al.* (2013) 'A new diamine containing disiloxane moiety and some derived Schiff bases: Synthesis, structural characterisation and antimicrobial activity', *Supramolecular Chemistry*, 25(8), pp. 490–502. doi: 10.1080/10610278.2013.794947.

(35) Zaltariov, M. F. *et al.* (2015a) 'Silicon-containing bis-azomethines: Synthesis, structural characterization, evaluation of the photophysical properties and biological activity', *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 138, pp. 38–48. doi: 10.1016/j.saa.2014.11.007.

(36) Zaltariov, M. F. *et al.* (2015b) 'Synthesis, characterization and antimicrobial activity of new Cu(II) and Zn(II) complexes with Schiff bases derived from trimethylsilyl-propyl-p-aminobenzoate', *Polyhedron*, 100, pp. 121–131. doi: 10.1016/j.poly.2015.07.030.

(37) Zaltariov, M. F. *et al.* (2016) 'Oxime-Bridged Mn6 Clusters Inserted in One-Dimensional Coordination Polymer', *Macromolecules*, 49(17), pp. 6163–6172. doi: 10.1021/acs.macromol.6b01149.

(38) Zaltariov, M. F. *et. al*. (2014) 'Tetranuclear Copper(II) Complexes with Macrocyclic and Open-Chain Disiloxane Ligands as Catalyst Precursors for Hydrocarboxylation and Oxidation of Alkanes and 1-Phenylethanol', *European Journal of Inorganic Chemistry*, 2014(29), pp. 4946-4956. https://doi.org/10.1002/ejic.201402578.

(39) Zaltariov, M. F. și Cazacu, M. (2020) 'Coordination compounds with siloxane/silane-containing ligands capable of self-assembly at nano/micro scale in solid state and in solution' în Ruiz-Molina și van Eldik, (eds) *Advances in Inorganic Chemistry*. Elsevier Inc. 76, pp. 155-196. doi: 10.1016/bs.adioch.2020.03.003.

(40) Zaltariov, M. F., Vieru, V., *et. al.* (2017) 'A Bis(μ-chlorido)-Bridged Cobalt(II) Complex with Silyl-Containing Schiff Base as a Catalyst Precursor in the Solvent-Free Oxidation of Cyclohexane', *European Journal of Inorganic Chemistry*, 2017(37), pp. 4324-4332. https://doi.org/10.1002/ejic.201700875.