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Grau
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Treball Final de Grau

Synthesis and characterization of coordination complexes with imine ligands.

Síntesi i caracterització de compostos de coordinació amb lligands imina.

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June 2019

UNIVERSITAT DE BARCELONA

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Primer de tot agrair al Grup de Magnetisme i Molècules Funcionals per haver-me donat l’oportunitat de realitzar aquest projecte i a més a més aconsellar-me durant el treball a les reunions de grup.

Agrair a la meva companya de laboratori, la Rosa, que durant el treball al laboratori ha respost a tots els meus dubtes amb un somriure.

Volia agrair especialment a la meva tutora, la Carolina, per tots els coneixements que m’ha transmès i que sempre m’hagi guiat i ajudat amb les preguntes que m’han sorgit.

REPORT

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1. SUMMARY

Recent studies related to coordination chemistry have put in the spotlight multifunctional complexes, which have magnetic properties tuned for the metals that are coordinated to ligands with chromophore groups that have useful optical properties. The combination of these properties makes this type of compounds of special interest for applications in fields like quantum computing, nanotechnology or materials science.

It is due to these applications that different ligands have been synthesized in order to study their properties when they are coordinated with metals with an axial anisotropy, since these metals might provide the complexes the condition of SMM (single-molecule magnet).

Keywords: coordination chemistry, imine formation, Schiff bases, azo isomerization, crystal structure, multifunctional molecules.

2. RESUM

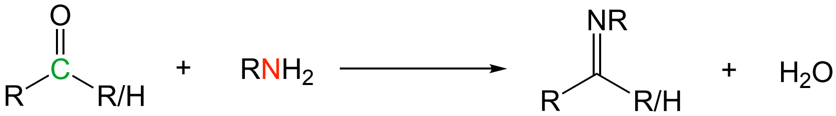
Estudis recents relacionats amb la química de coordinació han posat en el punt de mira els complexos multifuncionals, els quals tenen propietats magnètiques atorgades pels metalls que es coordinen a lligands amb grups cromòfors, que proporcionen les propietats òptiques. La combinació d'aquestes propietats fa que aquest tipus de compostos siguin d'especial interès per aplicacions en camps com la química quàntica, la nanotecnologia o la ciència de materials.

És degut a les diverses aplicacions que poden tenir aquests compostos que s'han sintetitzat diversos lligands per poder estudiar les seves propietats una vegada s'han coordinat amb metalls amb una anisotropia axial considerable, ja que són els metalls que proporcionen als complexos la condició de SMM (single-molecule magnet).

Paraules clau: química de coordinació, formació d'imines, bases de Schiff, isomerització de grups azo, estructura cristal·lina, molècules multifuncionals.

3. INTRODUCTION

Imines are organic compounds that contain a carbon–nitrogen double bond, when the third bond of the N is a bond to an organic group, they are called a Schiff base. The formation of the Schiff bases is usually product of the condensation reaction between an aldehyde or ketone with a primary amine *(Scheme 1)*.[1]



Scheme 1. Formation of Schiff bases: nucleophilic addition–elimination reaction.

This reaction is reversible, in order to favor the formation of the imine there are two options:[1] remove the water as it forms or make precipitate the imine. In this project the chosen method was the second, since the Schiff bases formed were insoluble in absolute ethanol.[2]

Schiff bases can act as ligands in coordination complexes. A coordination complex is formed by a central atom, that usually is a transition metal, attached to a group of atoms, which is known as ligand.[3] These ligands can be molecules or ions, both of them have in common the fact that they donate electrons to the central atom, in this work all the ligands were organic molecules with O and N as donor atoms.

The choice of the ligand is an important part, since it would affect the reactivity of the complex[3,4] and it can add some valuable properties like fluorescence and surface grafting ability.[5] The fluorescence of the ligands synthesized during this project has been studied since some ligands have fluorophore groups like naphthalene. Although the ligands prepared had not been deposited in a surface, it could be seen that ligands with aromatic groups, such anthracene, can be deposited in carbon based materials.[2]

These properties combined with the ones that the metal provides, gives us a multifunctional molecule that could have applications in fields like nanotechnology and biotechnology. Since the transition metals provide interesting magnetic properties due to their unpaired electrons, the metals used during this project were Co(II), Cu(II), Mn(II) and Mn(III). Also, was used Dy(III), the lanthanides are also interesting since they can provide luminescent properties due to their f–f transitions, which are forbidden by Laporte's rule, but it has been reported that the combination with a fluorescent ligand can result in a molecule that can emit light in the visible and the near IR due to the metal,[6,7] this effect is known as antenna effect.

Deepening in the magnetic properties, these complexes have a huge interest because they can act as a single–molecule magnet (SMM). An SMM is a molecule that is able to maintain the magnetic moment after the field is remove. The slow relaxation time of the magnetization is thanks to high spin value at fundamental state and high axial zero–field splitting, induced by crystal field distortions and spin–orbit interactions.[8] For this reason, transition metals with strong anisotropy were used in this project.

The first SMM was Mn_{12}–acetate[9], in *Figure 1* is shown its structure.[10]

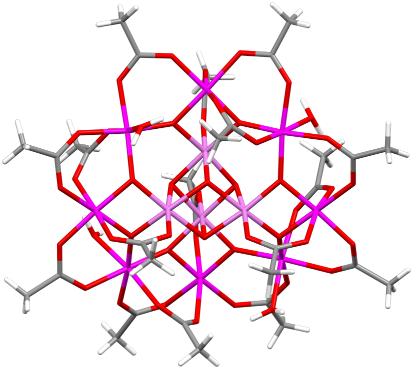


Figure 1. Mn_{12}–acetate structure.[9] Mn(III) are shown in dark pink and Mn(IV) in light pink.

The combination of a large negative value of the axial zero–splitting parameter (D) with a high spin value at ground state (S) arises in a good candidate to obtain an SMM, since they give a high barrier between the two possible orientations of the spin, this barrier is obtained from the splitting of S into levels, which is caused by the axial anisotropy.[11]

At high temperatures this barrier is not a problem for the system returns to the equilibrium, so the time of relaxation of the magnetization decreases, therefore, actually these molecules only have these properties below a blocking temperature, usually near to the absolute zero. One of the actual objectives is to obtain an SMM with a higher blocking temperature (T_B, temperature at which the magnetization is lost). Recently a dysprosium metallocene $[(\eta^5\text{–Cp*})\text{Dy}(\eta^5\text{–Cp}^{iPr5})][\text{B}(\text{C}_6\text{F}_5)_4]$ with a T_B = 80K was achieved.[12]

There are other ways of relaxation of the magnetization since these molecules are in the order of nanometers had been observed quantum phenomena, like tunneling as pathway of relaxation. This is sustained by the hysteresis loop of SMMs, like the Mn_{12}–acetate[13] or the Fe_8[14], that show a hysteresis loop with steps.

Although the molecules synthesized are expected to show these properties, since all of them have $S \neq 0$, the magnetism was not measured during the project.

The synthesis of these complexes not always have a predictable product, this is why some obtained complexes were unexpected respect to the synthesis that was proposed at first instance. This type of synthesis was termed as serendipitous assembly,[15] it considers not strictly design the complex and testing with different molar relations, ligands, metals, etc,.

In this work, for those syntheses that give an unexpected product an optimized synthesis was designed and performed.

4. OBJECTIVES

The objective of this project was to obtain multifunctional molecules, for achieve it, symmetric and asymmetric imine ligands and their coordination complexes were synthesized and characterized. The metals used for obtain the complexes were those with strong axial anisotropy, like Co(II), Mn (II), Dy (III) and Cu(II).

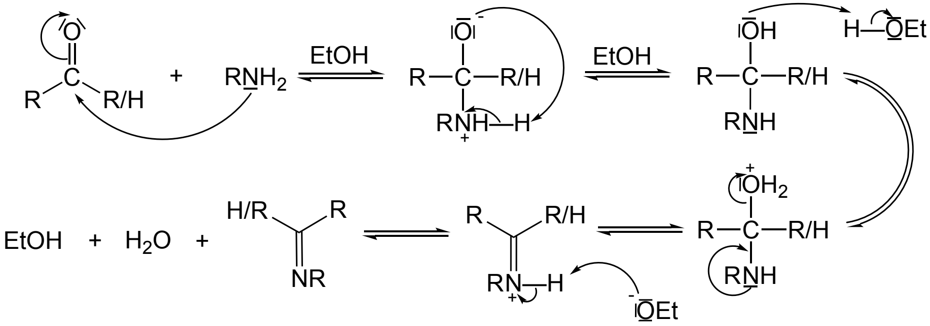
Specifying:

- Synthesis and characterization of ligands: AZO1, ASYML, SYML2.
- Synthesis and characterization of the complex AZO1 – M, where M = Co, Cu, Dy and Mn.
- Synthesis and characterization of the complexes ASYML – M, where M = Co, Cu, Dy and Mn.
- Synthesis and characterization of the complexes SYML1 – Mn and SYML2 – Mn.

5. RESULTS AND DISCUSSION

5.1. SYNTHESIS OF LIGANDS

The synthesis of the ligands performed in this project have similar reaction conditions because in all the cases the type of reaction performed is an imine formation.[1] In the synthesis performed for obtaining an imine, a primary amine was dissolved in the convenient solvent and the carbonyl compounds used were aldehydes in all the experiments. In the *Scheme 2* is shown the possible mechanism followed in the reactions where the solvent was ethanol. The imines prepared are shown in the *Figure 2*.



Scheme 2. Schiff bases formation mechanism.

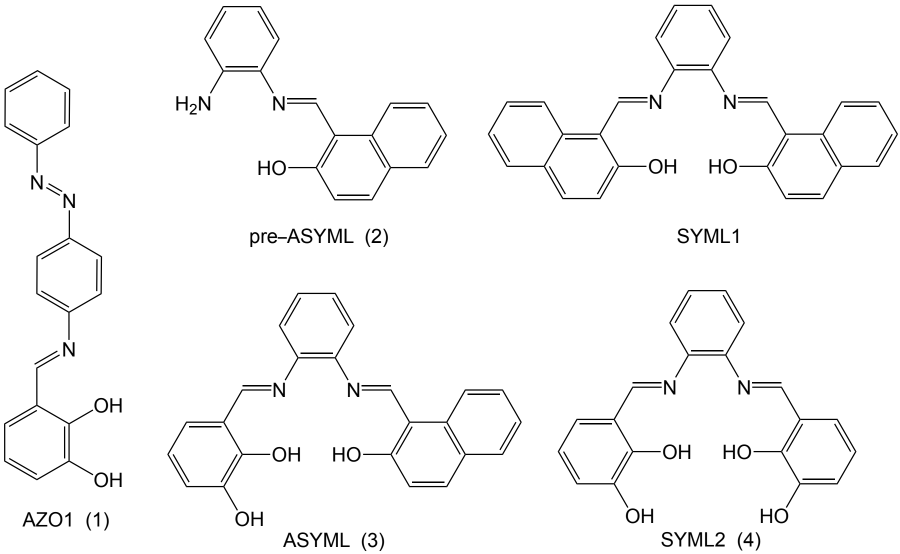
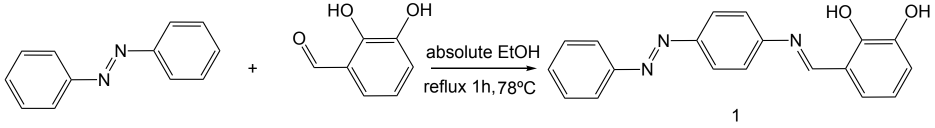

AZO1 (1)
pre–ASYML (2)
SYML1
ASYML (3)
SYML2 (4)

Figure 2. Ligands used during this project.

For this work the amines used were: (E)-4-(phenyldiazenyl)aniline, that provides asymmetric ligands and benzene-1,2-diamine, that can provide both type of ligands (symmetric and asymmetric) depending on whether one or two different aldehydes are added. The aldehydes used were: 2,3-dihydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde. The solvents used were absolute ethanol and dry THF. Absolute ethanol was chosen for the synthesis of **AZO1** (**1**), **ASYML** (**3**), and **SYML2** (**4**). In the case of **pre–ASYML** (**2**) dry THF was used.

All the spectra of the products are shown at *Appendix 3*.

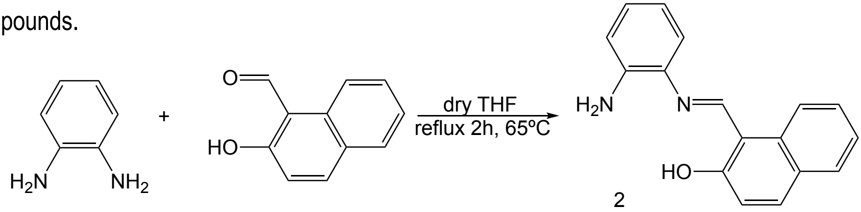
Analyzing the spectra obtained for AZO1 (**1**), at the IR spectrum, a band can be observed at 1625 cm^{-} that corresponds to the stretching of C=N bond,[16] also can be seen the band of N=N (st) at 1462 cm^{-} that is present in the azobenzene IR spectrum.[17] There are the typical bands around 1610–1450 cm^{-} due to the C–C (st) of the aromatic rings and bands between 850 and 685 cm^{-}, these correspond to the bending of C–H bond. Finally, a strong band is observed at 1219 cm^{-} caused by the bending of O–H bond of the phenols.[16] Moving forward to the ^{1}H NMR spectrum, although the molecule has 15 protons, the sum of the integration is 14, this is because only is seen one of the OH, at 13.60 ppm. At 8.69 ppm appears a singlet that integrates to one corresponding to the H attached to the imine group. The aromatic protons appear between 8.04 and 6.85 ppm, which is expected. MS spectrum gives the expected molecular peak 318.13. Although the emission fluorescence spectra show a band at 400 nm (λ_{ex} = 350nm, λ_{ex} = 280nm), the ligand **1** is not fluorescent, since the excitation spectrum at 400 nm was done and it does not show any signal.



Scheme 3. Formation of AZO1 (1).

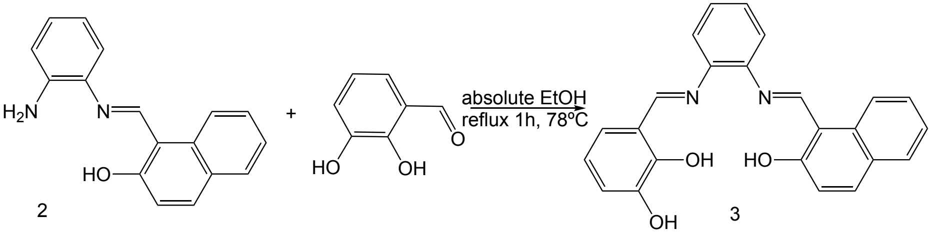
As it has been indicated before, ASYML (**3**) was prepared by two different methods; the *method A* consisted in a two-steps synthesis, where the first step was to react the benzene-1,2-diamine with the 2-hydroxy-1-naphaldehyde, obtaining **pre–ASYML** (**2**) and then it was reacted with 2,3-dihydroxybenzaldehyde for obtain ASYML (**3**) and *method B* was a single step reaction.

In the synthesis of ligand **3** by following the *method A* dry THF was used as solvent in the first step in order to avoid the formation of SYML1, as it is observed in the MS spectrum, the molecular peak is 263.12, corresponding with the expected for pre–ASYML (**2**), and only appears a small peak at 417.16, which is indicating the formation of a small quantity of SYML1. SYML1 is a symmetrical ligand synthesized and described before by the GMMF group.[7] Its structure is shown in *Figure 1*. Also, a TLC analysis was done, the product obtained was compared to pure SYML1 and **3** and it shown that the product was a mixture of these compounds.



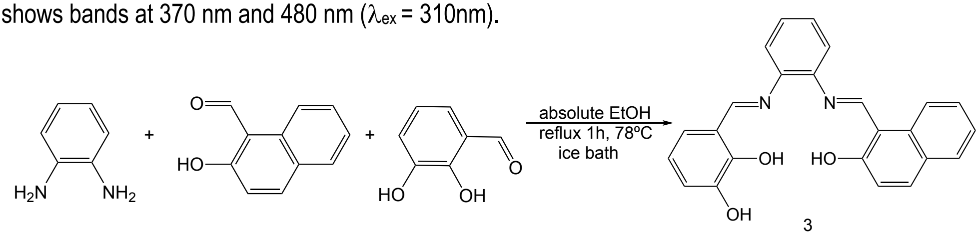
Scheme 4. Formation of pre–ASYML (2).

The product obtained in the reaction between pre–ASYML (**2**) with impurities of SYML1 and 2,3-dihydroxybenzaldehyde was a mixture of ASYML (**3**) and SYML1 as can be observed after analyzing the spectra of the product. As in the previous step, the MS spectrum of the product shows both peaks: 383.14 that corresponds to **3** and 417.16, the expected if the product was the symmetric ligand SYML1. The ^{1}H NMR spectrum could not be assigned since the obtained peaks were a mixture of the two species.



Scheme 5. Formation of ASYML (3) (*method A*).

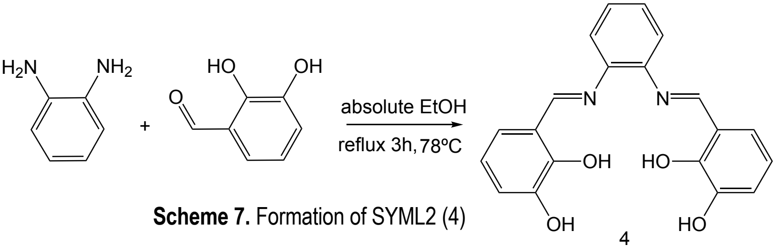
The product of *method B* (Scheme 6) was pure **3**, the IR spectrum shows the bands between 834 and 729 cm^{-} caused by the bending of C–H bond of the aromatic groups. But the most significant band is the one that appears at 1610 cm^{-} that confirms the presence of imines. ^{1}H NMR spectrum has all the three expected peaks of the OH groups (15.30, 13.16 and 9.35 ppm) and the characteristics peaks of the imine H, the one that corresponds to imine attached to the dihydroxylbenzene at 8.68 ppm as a singlet, and the other one at 8.08 ppm that appears like two different peaks, due to the rotation around the bond between the C of the imine and the C of the naphthalene group. The base peak of the MS spectrum (383.14), that was the expected, since the molecular weight of **3** is 382 g/mol. The emission fluorescence spectrum shows bands at 370 nm and 480 nm (λ_{ex} = 310nm).



3

Scheme 6. Synthesis of ASYML (3) (*method B*)

Finally, all the spectra recorded of SYML2 (**4**) coincides with the expected, an indicative that the obtained product was pure. The IR spectrum shows the previously commented band at 1610 cm^{-}, corresponding to the imine groups. In this case the molecule has a symmetry plane, so the ^{1}H NMR spectrum integrates to 8 protons. All the 5 types of aromatic hydrogens show up between 6.80 and 7.40 ppm, meanwhile the imine H appear at 8.63 ppm as a singlet. The hydroxyls are at 9.83 ppm and 13.47ppm, the ones that are nearest to the imine are the ones with a larger value of chemical shift. The MS spectrum gives the expected molecular peak, 349.12. The emission fluorescence spectrum shows bands at 400 nm and 460 nm (λ_{ex} = 335nm).

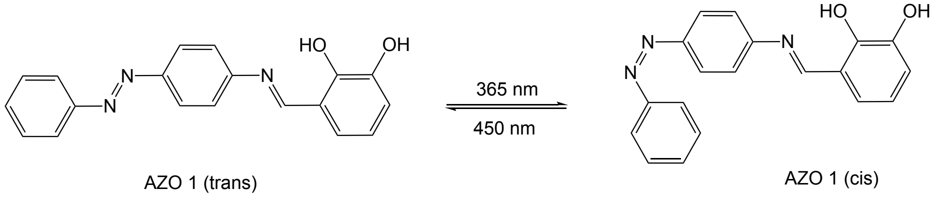


Scheme 7. Formation of SYML2 (4)

4

5.2. CIS/TRANS ISOMERIZATION OF AZO1

The stable form of AZO1 (**1**) is the trans isomer, as it was seen by single crystal X–ray diffraction, but as it is reported in the literature,[18] the cis isomer can be obtained by irradiating the stable form with ultraviolet light. To be able to observe this isomerization *(Scheme 8)*, a solution of **1** in acetonitrile was irradiated with a xenon lamp directly in the cuvette and after the irradiation the UV–Vis spectrum was recorded.



Scheme 8. Cis/trans isomerization of AZO1 (1).

The bands of trans–AZO1 have an intense absorption band at 360 nm due to the $\pi\rightarrow\pi^*$ transition. Meanwhile, the less intense $\pi\rightarrow\pi^*$ transition of cis–AZO1 take place at 270 nm.[18] These facts can be observed in *Figure 3*, where the absorption curve of trans–AZO1 before any irradiation is represented in blue and the band at 360 nm is the most intense. After irradiation with ultraviolet light (λ = 365nm) the curve has change (yellow) (*Figure 3*), the band that corresponds to the $\pi\rightarrow\pi^*$ transition of trans–AZO1 is less intense than in the previous spectrum, contrary, the band at 270 nm caused by the $\pi\rightarrow\pi^*$ transition of cis–AZO1 has become more intense. Finally, part of the trans isomer can be recovered by irradiating with visible light (λ = 450nm). This measure (pink curve) (*Figure 3*) was made after irradiating only with light of an exact wavelength at 450 nm, at normal conditions the isomerization to the stable form could be faster.

After, this isomerization was performed in presence of $CuCl_2 \cdot 2H_2O$ in order to see if there were changes in the absorbance curves respect to the free ligand **1**. When the salt of copper is added the curve (green) (*Figure 3*) is shifted to larger wavelengths and the bands become more intense. Also, a new band at 450 nm can be observed, due to the d–d transition of the Cu(II) (d^9) and a charge transfer band at 200 nm, which indicates that the metal is coordinated to the ligand **1**. The mixture was irradiated with ultraviolet light (λ = 365nm) (orange curve) (*Figure 3*), and the changes in the curve were alike the ones suffered by the free **1** once it was irradiated with this light, which indicates that ultraviolet light also can induce the isomerization from trans to cis form of the ligand when the metal is present. But, unlike to what occurred when the cis form of **1** was irradiated with visible light, in presence of Cu(II), both bands, the one at 380 nm caused by the $\pi\rightarrow\pi^*$ transition of the ligand **1** at trans form and the other at 315 nm due to the $\pi\rightarrow\pi^*$ transition of the cis form become less intense (purple curve) (*Figure 3*).

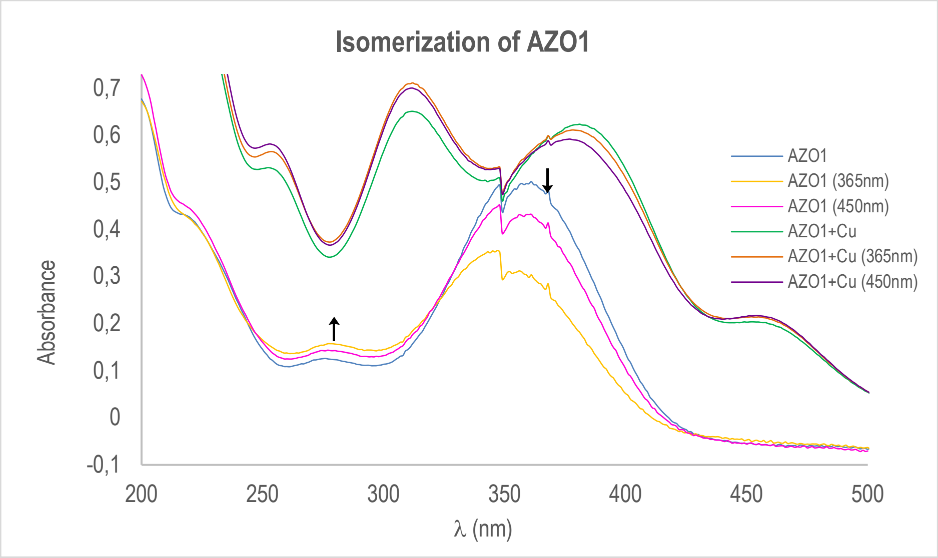


Figure 3. Isomerization of trans–AZO1 (blue) to cis–AZO1 (yellow) and recuperation of trans–AZO1 after time and irradiation with visible light (pink). AZO1 in presence of $CuCl_2$ (green), after irradiating the mixture with ultraviolet light (orange) and after irradiating the mixture with visible light (purple). The arrows are indicating that as the amount of trans–AZO1 (at 360 nm) decreases the cis–AZO1 (at 270 nm) increases.

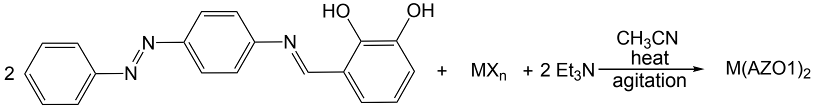
Although AZO1–Cu could not be isolated, the data shown below is promising, so further studies are necessary in order to know how to properly obtain the complex and then characterized it and observe in detail its properties.

5.3. SYNTHESIS OF THE COORDINATION COMPLEXES

The ligand AZO1 (**1**) was reacted with $CuCl_2 \cdot 2H_2O$, $CoCl_2$, $Dy(NO_3)_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$. At first, these reactions were performed in non-stoichiometric conditions by dissolving **1** in chloroform, but no change of color was observed, even after adding Et_3N and heating. In the cases which the salts of Dy(III) and Mn(II) were added, crystals were obtained, but the data obtained by crystal X–ray diffraction shows the free ligand **1**.

After these experiments, an orange/red solution of known concentration ($2 \cdot 10^{-3}$M) of **1** in acetonitrile was divided in four equal portions. To these solutions were added in stoichiometric quantities the correspondent salts of Cu(II), Co(II), Dy(III) and Mn(II), and in all the cases a change of color was observed, even without adding the Et_3N. The crystals obtained in these tests were not enough big for obtain crystallographic data.

The coordination of **1** to Mn was repeated in major scale, but using $Mn(OAc)_2 \cdot 4H_2O$ instead of $MnCl_2 \cdot 4H_2O$. The IR spectrum of the product shows changes in the fingerprint zone respect to the IR spectrum of free **1**, although crystals that confirm the existence of the Mn–AZO1 were not obtained.



Scheme 9. General reaction performed for attempt to form a complex with ligand **1**.

The ligand ASYML (**3**) was reacted with $CuCl_2 \cdot 2H_2O$, $CoCl_2$, $Dy(NO_3)_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$. In all the cases the reactions were performed in stoichiometric quantities. With the product obtained by *method A* dissolved in acetonitrile, tests with the salts of Cu(II), Dy(III) and Mn(II) were performed and the addition of each salt to a solution of **3** changed the solution color in the three cases. The crystals formed in the tests with manganese salt were analyzed, but it was seen that the product was not the complex ASYMLH–Mn, instead it was **SYML1–MnCl** (**5**). But this is not so rare, since the product of *method A* was a mixture of **SYML1** and **3**.

The ligand **3** (*method B*, pure) dissolved in methanol, was reacted with the salts of Co(II), Cu(II), Dy(III) and Mn(II), in all the cases a change of color was observed and crystals were obtained, but in the case of Co the crystals were too small for be able to obtain the crystal structural data, the performed MS and IR spectra show that it is a mixture of SYML1 and **3**. For the tests performed with Cu and Mn salts, complexes were obtained, with Cu the complex obtained was the expected one; **ASYMLH–Cu** (**6**), meanwhile, the reaction between **3** and $MnCl_2 \cdot 4H_2O$ gives an unexpected complex; **SYML2–Mn** (**7**). Finally, the crystals obtained in the tests with the dysprosium salt were a rotamer of the free ligand; **SYML1**. The obtained complexes are shown in *Figure 4*.

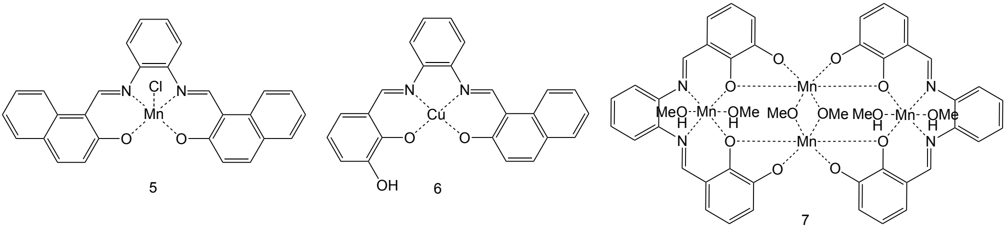


Figure 4. Coordination complexes obtained during this project.

These results may lead to think that the asymmetric ligand in solution and in the presence of some metal salts is not stable since only in one case was obtained a complex (**6**) with the asymmetric ligand and with a poor yield.

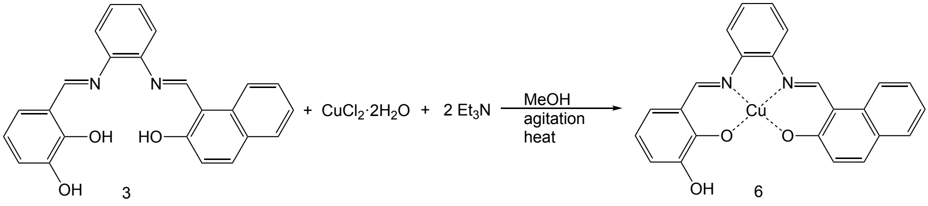
As it was explained before, the formation of imines is a reversible reaction and in order to avoid go back to the reagents, they were precipitated. But, when the asymmetric ligand is redissolved in methanol and the corresponding hydrated salt is added, the equilibrium (*Scheme 2*, but with MeOH instead of EtOH) can take place. Besides this, in the case where was used $MnCl_2 \cdot 4H_2O$, has been seen that the manganese suffered an oxidation form Mn(**II**) to Mn(**III**), which could shift the equilibrium to the aldehyde and the amine, since the oxidation of Mn(**II**) with O_2 produces OH^- (*Scheme 10*).

$$4\ Mn^{2+} + O_2 + 2\ H_2O \rightleftharpoons 4\ Mn^{3+} + 4\ OH^-$$

Scheme 10. Oxidation of Mn(II) to Mn(III) with the air.

In this case, the hydroxyl group and the MeOH are in acid/base equilibrium with the formation of water and methoxy group,[1] which means that there is more water present and therefore the return to the amine and the aldehydes is favored. Once the benzene-1,2-diamine and the aldehydes (2-hydroxy-1-naphthaldehyde and 2,3-dihydroxybenzaldehyde) are recovered, there is still the equilibrium between them and the formation of imines and finally what is obtained is the diimine that comes from the reaction between the diamine with two equivalents of the same aldehyde, 2-hydroxy-1-naphthaldehyde in the case of **SYML1**; 2,3-dihydroxybenzaldehyde in the case of SYML2–Mn (**7**).

Back to ASYMLH–Cu (**6**) complex, a MS and IR spectra were recorded. The MS spectrum shows a molecular peak at 444.06, according to the mass of this complex (443 g/mol) and the IR spectrum only have changes in the fingerprint zone, like it was expected. At *Scheme 11* is shown the reaction of complexation for complex **6**.



Scheme 11. Complexation reaction performed in order to obtain ASYMLH–Cu (**6**).

To optimize the synthesis of SYML1–MnCl (**5**), the reaction was performed with an equivalent of **SYML1** (already prepared), one equivalent of $MnCl_2 \cdot 4H_2O$ and two equivalents of Et_3N. The solvent used was CH_3Cl. The product was characterized by MS and IR analysis and the complex obtained was indeed **5**. IR spectrum shows changes at fingerprint zone respect to the free ligand SYML1 and the base peak of the MS spectrum is at 469.08, that coincides with the result of subtract the atomic mass of the Cl to the molecular mass of the complex (504 g/mol).

Finally, to obtain SYML2–Mn (**7**) with a designed reaction, the ligand **4** was reacted with $MnCl_2 \cdot 4H_2O$ and Et_3N in a molar relation of 2:4:4, respectively. The solvent used was MeOH. The characterization of the product shows a base peak at MS spectrum of 401.04, which is not matching with the molecular mass of **7** (1102 g/mol), but this fact was not strange since this complex was large and what is seen at the MS spectrum is a fragment of the complex (*Figure 5*).The IR spectrum compared with free ligand **4** shows changes at fingerprint zone and slightly wider band of alcohol, it maintains the characteristic bands caused by the ligand, as the imine band.

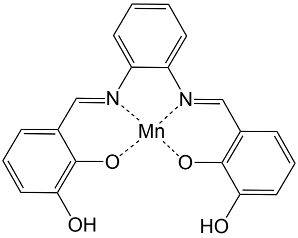


Figure 5. The observed fragment of the complex **7** at MS spectrum.

Further characterization by single crystal X–ray diffraction is needed to certainly know that the complexes **5** and **7** are formed with theses optimized synthesis.

5.4. CRYSTAL STRUCTURE DESCRIPTION

The crystal data of ligands and complexes is shown in *Table 1* and the oxidation state of the metals and the protonation of the ligands is shown at *Table 2A* and *Table 2B*, respectively. AZO1 (**1**) and SYML2 (**4**) were obtained by slow evaporation of the solvent, meanwhile ASYMLH–Cu (**5**), SYML1–MnCl (**6**) and SYML2–Mn (**7**) were obtained by performing a liquid–liquid slow diffusion with hexanes. These two last crystalline structures of symmetric complexes were obtained unexpectedly, since the salt of manganese was added to a solution ASYML (**3**).

Table 1. Crystal data and structure parameters of the products

Sample	**AZO1**	**SYML2**	**ASYMLH – Cu**	**SYML1 – MnCl**	**SYML2 – Mn**
	1	**4**	**5**	**6**	**7**
cristal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P\ 2_1/n$	$P\ 2_1/n$	P c c n	$P\ 2_1/c$	P - 1
a [Å]	9.9609 (14)	6.1465 (3)	21.339 (3)	20.567 (10)	13.0498 (5)
b [Å]	5.7314 (18)	14.3296 (6)	22.875 (3)	13.798 (7)	13.4777 (5)
c [Å]	27.239 (5)	21.8627 (7)	8.3933 (11)	16.136 (8)	16.4518 (2)
α [º]	90	90	90	90	89.486 (2)
β [º]	100.54	98.039 (3)	90	112.878 (14)	75.109 (2)
γ [º]	90	90	90	90	68.798 (2)
V [$Å^3$]	1528.8 (5)	1906.68	4097.02	4218.91 (4)	2594.06 (17)
Z	2	4	8	8	4
$[I>2\delta(I)]$	wR = 0.0485	wR = 0.1852	wR = 0.1759	wR = 0.2714	wR = 0.0617

Table 2A. Oxidation state of the metals at the complexes

Complex	**Metal**	**BVS Cu(I)**	**BVS Cu(II)**
ASYMLH – Cu (5)	Cu	–	**2.40**
Complex	**Metal**	**BVS Mn(II)**	**BVS Mn(III)**
SYML1 – MnCl (6)	Mn	3.13	**2.98**
SYML2 – Mn (7)	Mn1	3.42	**3.16**
	Mn2	3.43	**3.17**
	Mn3	**2.28**	2.13
	Mn4	**2.29**	2.15

* The values in bold are the ones that correspond to the oxidation state of the metal at the indicated complex in each case. These values were calculated with the formula (1) shown at Appendix 2.

Table 2B. Protonation state of the ligands at the complexes

Complex	Oxygen	ROH	RO⁻
ASYMLH – Cu (5)	O1	–	1.82
	O2	–	1.82
	O3	0.99	–
SYML1 – MnCl (6)	O1	–	1.98
	O2	–	1.96
SYML2 – Mn (7)	O1	–	1.91
	O2	–	1.90
	O5	–	1.88
	O6	–	1.90
	O3	–	1.67
	O4	–	1.68
	O7	–	1.69
	O8		1.71
	O11	1.13	–
	O12	1.12	–
	O13	1.14	–
	O14	1.16	–
	O9	–	2.06
	O10	–	2.07

* For protonated oxygens the value of the BVS is around 1, meanwhile for the alkoxydes the value of the BVS is around 2. These values were calculated with the formula (2) shown at Appendix 2.

The crystal structure of free ligand AZO1 (**1**) is shown in the *Figure 6*. It has 5 donor atoms (2O, 3N), but in this work it would coordinate through the N of the imine group and the oxygen of the nearest hydroxyl group. The distance between this O and the N of the imine is 2.559 Å, shorter than the expected due to intramolecular hydrogen bond.[19,20] A similar molecule, without the hydroxyl group at meta position respect to the imine group, was described before.[21] The bond distance of the C=N is 1.295 Å, which is the expected one for an imine group.[22] Meanwhile, the C–C bond between the imine C and the next C has a double bond character, its bond distance (1.436 Å) is between the standard values of simple (1.54 Å) and double bond (1.34 Å).[22] The azo group (N=N) has a distance bond of 1.25 Å, which is the expected distance for a double bond between N=N.[22]

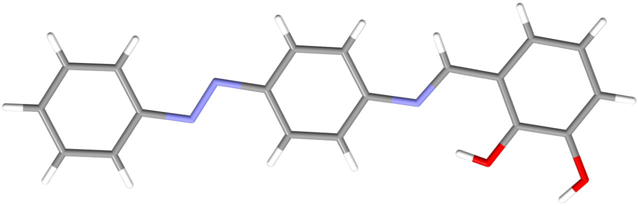


Figure 6. Crystal structure of AZO1 (1).

The crystal structure of free ligand SYML2 (**4**) is shown in the *Figure 7*, where it can be seen that it is not planar, since in that case the oxygens of each side will be closer to the other one and it would not be stable. This structure was described before in previous studies.[23] The torsion angle O–N–N–O is 36.12º. This molecule has 6 donor atoms (4O, 2N). There are to imine groups, with a C=N distances of 1.272 Å and 1.287 Å. The C–C bonds, between the imine C and the next C, have a double bond character as their distances indicate 1.434 Å and 1.464 Å. There are two intramolecular hydrogen bonds, between the N and the H of the nearest hydroxyl group, with a bond distances between the two heavy atoms of 2.529 Å and 2.628 Å.

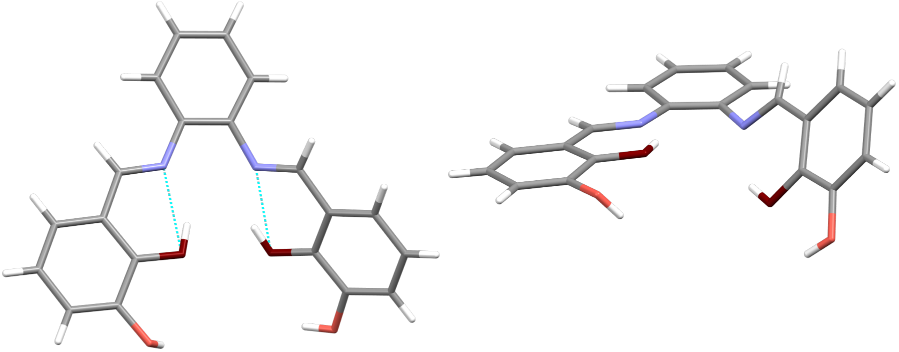


Figure 7. Crystal structure of SYML2 (4).

The crystal structure of free ligand ASYMLH–Cu (**5**) is shown in the *Figure 8,* the ligand has 5 donor atoms (3O, 2N), but it is coordinated to the cooper through the two nitrogen and the nearest two oxygens, therefore the Cu(II) has a coordination number of 4 and it is in a square–planar environment. A similar complex was synthesized,[24] where the ligand is SYML1 instead of the one prepared in this work. The two imine groups have a distance of 1.316 Å, in the case of the imine attached to the naphthalene group, and 1.285 Å for the other one. The torsion angle

O–N–N–O is 1.60º. The angles around the metal are 85.17º (N–Cu–N) and 87.70º (O–Cu–O). The intramolecular distances between the metal and the donor atoms are 1.918 Å and 1.932 Å for Cu–N bonds; 1.887 Å and 1.881 Å for Cu–O bonds. At the packing of the molecules is observed an intermolecular π–π stacking with a distance between the rings in the range of 3.229 Å to 3.400 Å.

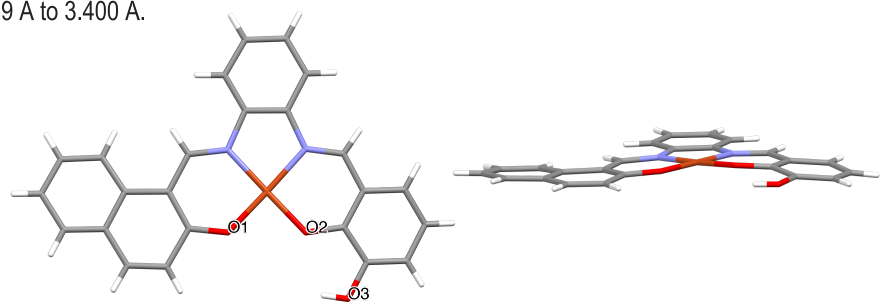


Figure 8. Crystal structure of ASYMLH–Cu (5).

The crystal structure of SYML1–Mn (**6**) is shown in the *Figure 9*. The ligand has 4 donor atoms (2O, 2N), through these atoms the metal is coordinated to the ligand and it has one more coordination position, occupied by a chloride. This complex was synthesized before with iron as central metal.[25] There are two imine groups, with a C=N distances of 1.338 Å and 1.117 Å, this last value is abnormally short for a C=N bond, this is due to the poor structural data obtained for this crystal. The Mn (III) is above the plane of the donor atoms of the ligand, stabilized by the chloride atom. The torsion angle O–N–N–O is 5.74º. The angles around the metal are 85.18º (N–Mn–N) and 91.35º (O–Mn–O). The intramolecular distances between the metal and the donor atoms are 2.022 Å and 2.098 Å for Mn–N, 1.890 Å and 1.897 Å for Mn–O bond and 2.400 Å for Mn–Cl bond.

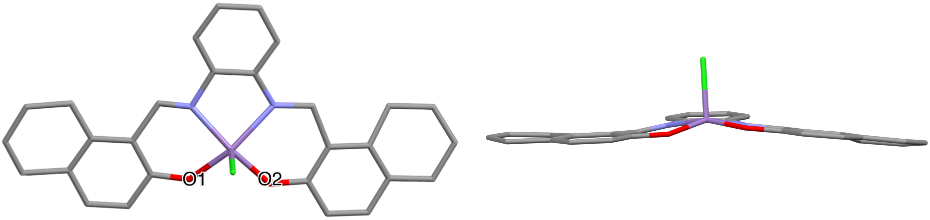


Figure 9. Crystal structure of SYML1–MnCl (6).

SYML2–Mn (**7**) crystal structure and an image of the monocrystal are shown in the *Figure 10*. Although there are similar structures[26] to this compound, this complex was not synthesized before. It contains four manganese, the two Mn forming part of the methoxy-bridges are Mn(III), meanwhile, the other two are Mn(II). The two Mn(II) are hexacoordinated in a distortional octahedral environment. The two MeOH groups with an intramolecular distance to the metal of 2.268 Å and 2.295 Å are positioned in trans respect to each other. The donor atoms of the SYML2 ligand are two nitrogen and the nearest two oxygens. The Mn–O distances are between 2.067 Å and 2.077 Å and Mn–N distances are between 2.177 Å and 2.187 Å. The angles around the metals are 76.58º (N–Mn–N) and 113.53º (O–Mn–O) for one of the Mn(II) and 76.67º (N–Mn–N) and 111.43º (O–Mn–O) for the other one.

The two Mn(III) are hexacoordinated. Each one is coordinated to six oxygens, four are provided by the ligands, and both metals are coordinated to the same two methoxy groups. Of the four oxygens from the ligands, two of them are also coordinated to Mn(II) and they are in trans respect each other, and the other two are in cis respect each other. The intramolecular distances of: Mn–O (oxygen coordinated also to Mn(II)) are in the range of 2.165 Å and 2.198 Å, Mn–O are in the range of 1.912 Å and 1.922 Å and for the Mn–OMe are in the range of 1.936 Å and 1.945 Å. The Jahn–Teller effect is confirmed by these distances, since there are two pairs of distances that are around the same value (~1.9 Å), meanwhile the other pair of distances at longer than the previous (~ 2.1 Å) and they are in trans one respect the other, distorting the octahedron by elongating it. The torsion angles (O–N–N–O) are 14.77º and 14.50º. The two ligands are rotated 136.5º respect each other.

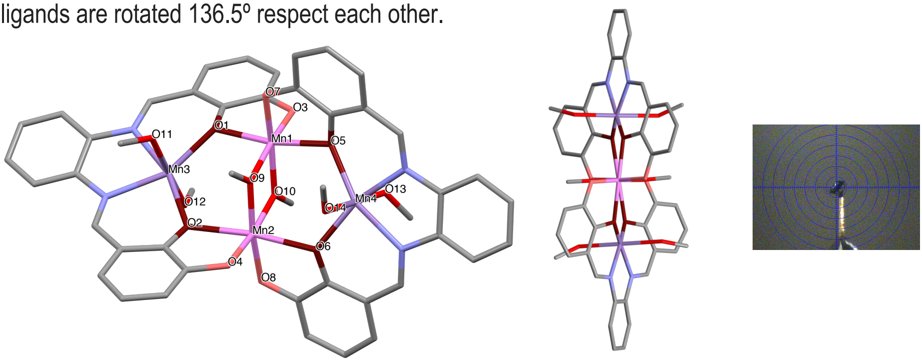


Figure 10. Crystal structure of SYML2–Mn (7).

6. EXPERIMENTAL SECTION

6.1. MATERIALS, INSTRUMENTS AND METHODS

The reagents used for the synthesis of the ligands and supplier are shown in the *Table 3*. All the reagents were purchased in commercial sources and were used as received. The salts used for the synthesis of coordination complexes are shown in the *Table 4*. Also, Et_3N was used as base, in order to deprotonate the ligands. The solvents, its quality and supplier are shown in the *Table 5*. SYML1 was already prepared in the laboratory.

Table 3. Reagents used for the synthesis of the ligands

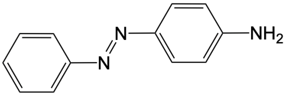
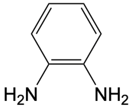
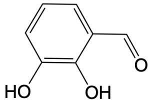
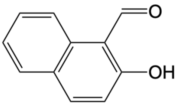
Name	Structure	Supplier
(E)-4-(phenyldiazenyl)aniline		Sigma Aldrich
benzene-1,2-diamine		Sigma Aldrich
2,3-dihydroxybenzaldehyde		Sigma Aldrich
2-hydroxy-1-naphthaldehyde		Sigma Aldrich

Table 4. Salts used for the synthesis of the complexes

Formula	Supplier
$CoCl_2$	Acros
$CuCl_2 \cdot 2H_2O$	–
$Dy(NO_3)_3 \cdot 6H_2O$	Streamlight
$MnCl_2 \cdot 4H_2O$	Sigma Aldrich
$Mn(OAc)_2 \cdot 4H_2O$	Sigma Aldrich

Table 5. Solvents

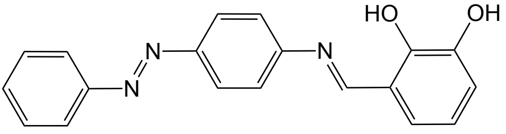
Solvent	Quality	Supplier
Acetone	HPLC quality ≥99.8%	Sigma Aldrich
Acetonitrile	HPLC quality ≥99.9%	Sigma Aldrich
Chloroform	Reagent plus ≥99.8%	Sigma Aldrich
Diethyl ether	ACS reagent ≥99.7%	Sigma Aldrich
Ethanol	ACS reagent ≥99.5%	Panreac
Hexane	ACS reagent ≥99%	Sigma Aldrich
Methanol	ACS reagent ≥99.8%	Sigma Aldrich
THF	HPLC quality ≥99.9%	Scharlau

The IR spectra were recorded on IR Avatar 330 FT–IR Thermo Nicolet 5700 with KBr plates and also using the ATR complement. The intensity of the signals is indicated as: (s) strong, (m) medium, (w) weak. The MS spectra were recorded on CCiT service. The NMR spectra were recorded on a Varian Mercury 400MHz, at 298K using $CDCl_3$. Coupling constants are given in Hz and the multiplicity of signals is indicated as: (s) singlet, (d) doublet, (t) triplet, (m) multiplet. Data of the single-crystal diffraction were recorded on Bruker APEX II Smart Quazar at GMMF facilities. The treatment of data and the image of the structure was done in Mercury computer program. The UV–Vis spectra were recorded on a Varian Cary 100 Scan UV–Visible Spectrophotometer. The lamp Asahi Spectra MAX–303 Compact Xenon Light Source was used for the experiment of isomerization of AZO1 ligand. The fluorescence spectra were recorded on an iHR320 Horiba Jobin Yvon imaging spectrometer. TLC analysis with aluminum plates coated with a layer of silica gel 60 F_{254}. Lamp: Spectroline Model ENF–240C/EF.

Slow liquid–liquid diffusion was the chosen method for obtain single crystals, this method is performed in a vial with the product dissolved in a solvent (A) and then a less dense solvent (B) is placed with a syringe in order to avoid the mixing them, over the solvent A. The solvents have to be miscible and the product has to be insoluble in the solvent B. As the solvent B diffuses into the solvent A, the solubility of the product decreases gradually, which allows a slow nucleation and crystals are formed.[27]

6.2. PREPARATION OF LIGANDS

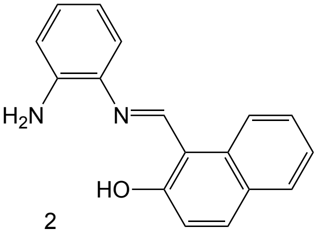
AZO1 (**1**) (3-((E)-((4-((E)-phenyldiazenyl)phenyl)imino)methyl)benzene-1,2-diol): 250 mg (1.267 mmol) of 4-aminoazobenzene were dissolved in 15 mL of absolute ethanol. 175.1 mg (1.267 mmol) of 2,3-dihydroxybenzaldehyde were added to the previous solution. The resulting orange solution was refluxed for 1h at 78ºC. The obtained purple precipitate was filtered and dried with ether. Yield: 51%



1

IR (KBr, cm^{-1}): 1625(s), 1575(s), 1462(s), 1360(m), 1275(m), 1219(s), 847(m), 773(m), 727(m), 688(w), 558(w). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 13.60 (s, 1H), δ 8.69 (s, 1H), δ 8.02 (d, J = 8.6 Hz, 2H), δ 7.94 (d, J = 7.0 Hz, 2H), δ 7.57–7.47 (m, 3H), δ 7.44 (d, J = 8.6 Hz, 2H), δ 7.08 (dd, J = 7.8, 1.42 Hz, 1H), δ 7.01 (dd, J = 7.9, 1.5 Hz, 1H), δ 6.87 (t, J = 7.8 Hz, 1H). **LRMS (ESI)**: ($C_{19}H_{15}N_3O_2$) MW = 317 g/mol Ms/z ($M+1H^+$) = 318.13. **UV–Vis**: 270 nm, 360 nm. **Fluorescence** (emission): 400 nm (λ_{ex} = 350nm, λ_{ex} = 280nm).

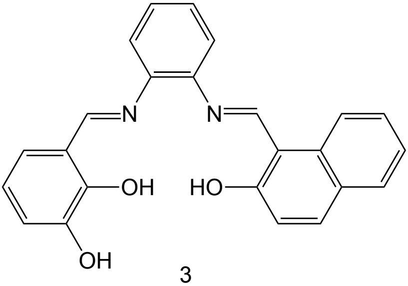
pre–ASMYL (**2**) ((E)-3-(((2-aminophenyl)imino)methyl)naphthalen-2-ol): 0.54 g (5 mmol) of benzene-1,2-diamine were dissolved in 30mL of dry THF. 0.86 g (5 mmol) of 3-hydroxy-2-naphthaldehyde were added to the previous solution. The resulting orange solution was refluxed for 2h at 65ºC. After two days it did not precipitate. The orange solution was refluxed for 2h at 65ºC in presence of zeolites. The color of the solution after the second reflux was a dark orange, almost black. This solution was left into the fridge 24h, but it did not crystallize. It was precipitated with 10-15 mL of hexane. A black solid was obtained, it was filtered and dried with diethyl ether. Yield: 37%



2

IR (ATR, cm^{-1}): 1056(m), 955(s), 765(m), 716 (m), 667(m), 650 (m). **LRMS (ESI)**: ($C_{17}H_{14}N_2O$) MW = 262 g/mol Ms/z (M+1H$^+$) = 263.12.

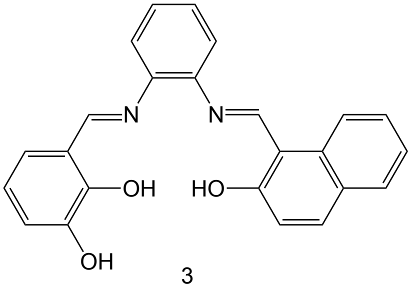
Method A **– ASYML** (**3**) (3-((E)-((2-(((E)-(3-hydroxynaphthalen-2-yl)methylene)amino)-phenyl)imino)methyl)benzene-1,2-diol): 434 mg (1.65 mmol) of pre–ASYML were dissolved in minimum quantity of absolute EtOH. 229 mg (1.65 mmol) of 2,3-dihydroxybenzealdehyde were added to the previous solution. The resulting brown solution was refluxed for 1h at 78ºC. It was left to precipitate at room temperature for 1h. The brown/black solid obtained was filtered and dried with diethyl ether. Yield: 25%



3

IR (ATR, cm^{-1}): 1611(s), 1573(m), 1544(m), 1460(m), 1351(m), 1268(s), 1194(m), 1159(w), 965(w), 730(s). **LRMS (ESI)**: ($C_{24}H_{18}N_2O_3$) MW = 382 g/mol Ms/z (M+1H$^+$) = 383.14 and ($C_{28}H_{20}N_2O_2$) 417.16.

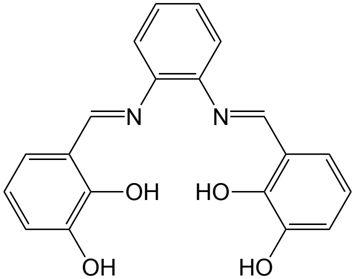
Method B – ASYML (**3**) (3-((E)-((2-(((E)-(3-hydroxynaphthalen-2-yl)methylene)amino)-phenyl)imino)methyl)benzene-1,2-diol): 0.39 g (3.62 mmol) of benzene-1,2-diamine were dissolved in minimum quantity of absolute EtOH. 0.565 g of 3-hydroxy-2-naphthaldehyde and 0.500 g (3.62 mmol) of 2,3-dihydroxybenzealdehyde were added to the previous solution. The resulting orange solution was refluxed for 1h at 78ºC. After this time the color of the solution changed to a more intense orange/red. The solution was cooled in ice bath, diethyl ether was added in order to make it precipitate. The red solid obtained was filtered and dried with diethyl ether. Yield: 55%



3

IR (ATR, cm^{-1}): 1610(s), 1586(m), 1544(m), 1485(m), 1347(m), 1273(s), 1194(m), 1155(w), 962(w), 754(s), 729(s). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 15.29 (d, J = 4.6 Hz, 1H), δ 13.16 (s, 1H) δ 9.35 (d, J = 5.0 Hz, 1H), δ 8.68 (s, 1H), δ 8.08 (d, J = 8.5 Hz, 1H), δ 7.80 (d, J = 9.1 Hz, 1H), δ 7.70 (d, J = 7.3 Hz, 1H), δ 7.51 (d, J = 8.1 Hz, 1H), δ 7.48–7.27 (m, 5H), δ 7.10 (d, J = 9.1 Hz, 1H), δ 7.06 (d, J = 7.9 Hz, 1H), δ 7.00 (d, J = 7.7 Hz, 1H), δ 6.85 (t, J = 7.9 Hz, 1H). **LRMS (ESI)**: ($C_{24}H_{18}N_2O_3$)MW = 382 g/mol Ms/z (M+1H$^+$) = 383.14. **UV–Vis**: 270 nm, 310 nm, 400 nm, 475nm. **Fluorescence** (emission): 370 nm and 480nm (λ_{ex} = 310nm).

SYML2 (**4**) (3,3'-((1E,1'E)-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))-bis(ben-zene-1,2-diol): 0.433 g (4 mmol) of benzene-1,2-diamine were dissolved in 15mL of absolute EtOH. 1.105 g (8 mmol) of 2,3-dihydroxybenzealdehyde were added to the previous solution. The resulting orange solution was refluxed for 2-3h at 78ºC, during the reflux the solution was changing to an intense red color. After the reflux an ice-bath is performed. The red solid obtained was filtered and wash with diethyl ether. Yield: 88%



4

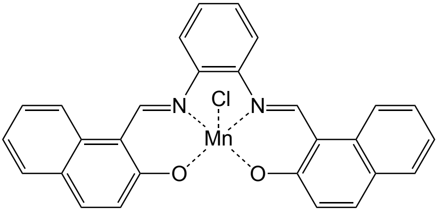
IR (ATR, cm^{-1}): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 13.47 (s, 1H), δ 9.83 (s, 1H), δ 8.63 (s, 1H), δ 7.38 (dd, J = 5.9, 3.4 Hz, 1H), δ 7.28 (dd, J = 5.9, 3.4 Hz, 1H), δ 7.05 (dd, J = 7.9, 1.5 Hz, 1H), δ 6.97 (dd, J = 7.8, 1.5 Hz, 1H), δ 6.84 (t, J = 7.8 Hz, 1H). **LRMS (ESI)**: ($C_{20}H_{16}N_2O_4$)MW = 348 g/mol Ms/z (M+1H$^+$) = 349.12. **UV–Vis**: 280 nm, 335 nm, 475 nm. **Fluorescence** (emission): 400 nm and 460 nm (λ_{ex} = 335nm).

6.3. ISOMERIZATION OF AZO1

1 mg of AZO1 were dissolved in 10 mL of acetonitrile. The solution was too concentrated; therefore, it was diluted to a concentration of $6 \cdot 10^{-6}$M of AZO1. The prepared solution of trans isomer of AZO1 was excited with ultraviolet light (λ = 365 nm) in order to obtain the cis isomer. After this irradiation, UV-Vis spectrum was collected. To recover the trans isomer, the solution was irradiated with visible light (λ = 450 nm), the UV-Vis spectrum was collected. Also, was performed an experiment following the previous procedure but adding $CuCl_2 \cdot 2H_2O$ to observe the isomerization process in presence of Cu(II).

6.4. PREPARATION OF COORDINATION COMPLEXES

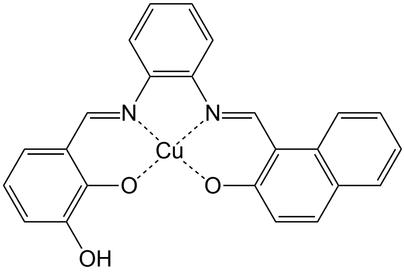
SYML1–MnCl (**5**): 100 mg (0.240mmol) of SYML1 were dissolved in 7 mL of $CHCl_3$ under conditions of agitation and heat, the resulting solution was orange. 47.6 mg (0.240 mmol) of $MnCl_2 \cdot 4H_2O$ were added to the previous solution, no color change was observed. 70 µL (0.480 mmol) of Et_3N were added, there was a change of color after 35min, from orange to a darker orange. The orange/brown solid obtained was filtered and then dissolved in MeOH for recrystallize by liquid-liquid slow diffusion with diethyl ether and hexane. Yield: 95%



5

IR (ATR, cm^{-1}): 1614 (w), 1595 (m), 1572 (m), 1529 (s), 1374 (m), 1359 (s), 1339 (m), 1303 (w), 1195 (m), 1172 (w), 980 (m), 829 (w), 753, 734 (s), 578 (w), 562 (s). **LRMS (ESI)**: ($C_{28}H_{18}N_2O_2$-MnCl) MW = 504 g/mol Ms/z it is not observed. ($C_{28}H_{18}N_2O_2$-Mn) ($M+1H^+$) = 469.08.

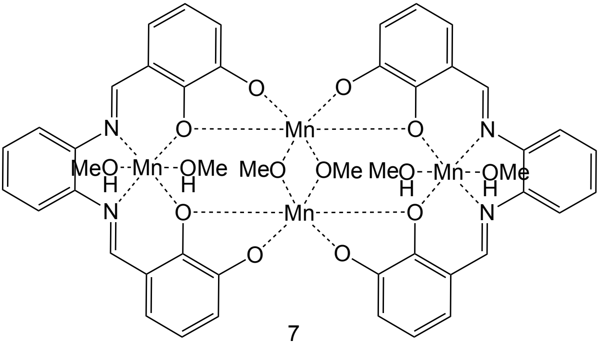
ASYMLH–Cu (**6**): 81.5 mg (0.213 mmol) of **3** were dissolved in 5 mL of MeOH under conditions of agitation and heat, the resulting solution was orange. 36.37 mg (0.213 mmol) of $CuCl_2 \cdot 2H_2O$ were added to the previous solution, a color change was observed, from orange to dark red. 60 µL (0.426 mmol) of Et_3N were added. The brown solid obtained was filtered and then dissolved in CH_3CN for recrystallize by liquid-liquid slow diffusion with hexane. Yield: 5%



6

IR (ATR, cm^{-1}): 1614 (w), 1600 (m), 1575 (m), 1535 (m), 1444 (m), 1397 (w), 1364 (s), 1285 (m), 1221 (w), 1193 (s), 1037 (w), 824 (w), 732, 720 (s). **LRMS (ESI)**: ($C_{24}H_{16}N_2O_3$-Cu) MW = 443.64 g/mol Ms/z (M+1H$^+$) = 444.06. (M+Na$^+$) = 467.06. (2M+H$^+$) = 889.10

SYML2–Mn (**7**): 100 mg (0.287 mmol) of **4** were dissolved in 15 mL of MeOH under conditions of agitation and heat, the resulting solution was red/orange. 113.68 mg (0.574 mmol) of $MnCl_2 \cdot 4H_2O$ were added to the previous solution gets a darker color. 80 µL (0.574 mmol) of Et_3N were added. The solution was heated and stirred for 5 minutes and after was added to a vial for perform a slow–evaporation. A dark brown solid was obtained. Yield: 80%



7

IR (ATR, cm^{-1}): 1607, 1578 (w), 1539(w), 1440 (m), 1248 (s), 1191 (m), 734 (m), 588 (m). **LRMS (ESI)**: ($C_{46}H_{50}N_4O_{14}$-Mn_4) MW = 1102 g/mol it is not observed. ($C_{20}H_{14}N_2O_4$-Mn) Ms/z (M+1H$^+$) = 401.04.

7. CONCLUSIONS

Although all the proposed ligands (AZO1 (1), ASYML (3) and SYML2 (4)) were successfully synthesized, the first designed synthesis for ASYML (3) (method A) caused more problems since it produces a mixture of the symmetrical and asymmetrical ligands, so a second synthetic method was proposed, which consisted in mixing all starting material and it provides a pure product. For AZO1 (1) has been seen that it can be isomerized to the cis form by irradiating with ultraviolet light and it can return to the stable form (trans) by irradiating with visible light.

The complexation synthesis of the complexes with symmetrical ligands, SYML1–MnCl (5) and SYML2–Mn (7), were achieved, but in the case of ASYML complexes only was obtained the complex with copper as a central ion; ASYMLH–Cu (6), and with a poor yield. This is due to the fact that the imine is not stable in solution since it suffers an equilibrium with the aldehyde and the primary amine. Finally, although AZO1 (1) was reacted with four different salts and in all the tests the color of the solution has changed, in any case was obtained crystallographic data that confirms the existence of these complexes, but some data obtained is promising; an IR spectrum of the product between the reaction of AZO1 (1) and $MnCl_2{\cdot}4H_2O$ was performed and it shows the bands of the free ligand with some changes at the fingerprint zone, with can be an indicative of the formation of a complex AZO1–Mn, and the UV–Visible data obtained of a solution of AZO1 (1) containing $CuCl_2{\cdot}2H_2O$ is interesting, it shows a shift and increase of the intensity of the bands respect to free AZO1 (1) which also can be indicating a complexation of the ligand with copper.

The main objective was to prepare multifunctional molecules, with magnetic and fluorescence properties. The fluorescence of the ligands was studied, the ligands ASYML (3) and SYML2 (4) present fluorescence, AZO1 (1) do not, but since the presence of an isomerization process that can be controlled still can be interesting to study more about it. Although the magnetic properties were not studied, for future research would be interesting; Mn(III) is a good option to obtain a mononuclear SMM due to Jahn Teller effect and a large negative value of the axial zero–splitting parameter, as has been seen before in the complex $Ph_4P[Mn(opbaCl_2)(py)_2]$,[28,29] with a similar geometry to SYML1–MnCl (5). In the case of SYML2–Mn (7), it is expected that the anisotropy be elevated since the Jahn Teller axis of the two Mn(III) are parallel one respect the other. Finally, although the Cu(II) has a poor anisotropy, it can have applications as a qubit.

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9. ACRONYMS

BVS: Bond Valance Sum

GMMF: Grup de magnetisme i molècules funcionals

Mn_{12}–acetate: $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$

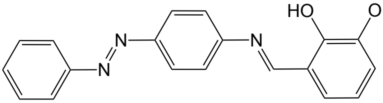
SMM: Single–Molecule Magnet

THF: Tetrahydrofuran

APPENDICES

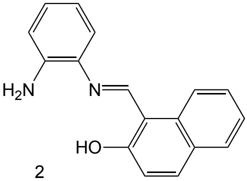
APPENDIX 1: PRODUCTS

(1) AZO1: 3-((E)-((4-((E)-phenyldiazenyl)-phenyl)imino)methyl)benzene-1,2-diol



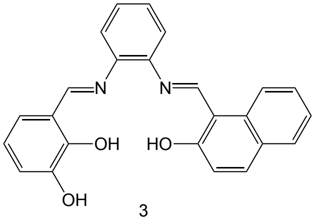
1

(2) pre–ASMYL: (E)-3-(((2-aminophenyl)imino) methyl)naphthalen-2-ol



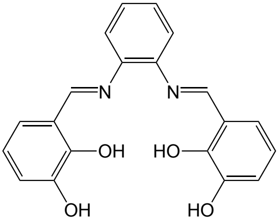
2

(3) ASYML: 3-((E)-((2-(((E)-(3-hydroxynaphthalen-2-yl)methylene)amino)phenyl)-imino)methyl)benzene-1,2-diol).



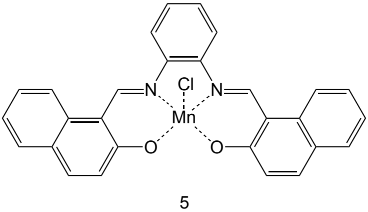
3

(4) SYML2: 3,3'-((1E,1'E)-(1,2-phenylenebis-(azaneylylidene))bis(methaneylylidene))bis-(benzene-1,2-diol)



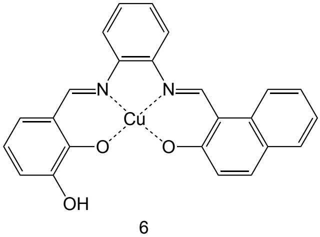
4

(5) SYML1–MnCl



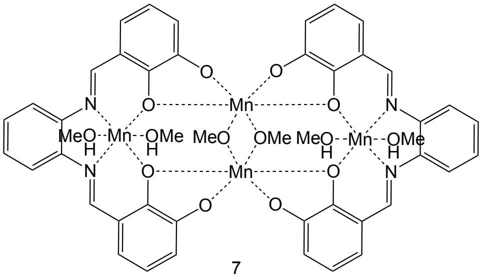
5

(6) ASYMLH–Cu



6

(7) SYML2–Mn



7

APPENDIX 2: BOND VALANCE SUM

To know the oxidation state of the metals of the complexes was use the BVS equation **(1)**,[30] where **V**$_i$ represents the oxidation state of the atom *i*, **r**$_{ij}$ is the bond length between the atom *i* and the atom *j* and **r**$_o$ and **B** are tabulated parameters.

$$V_i = \sum_j exp\left(\frac{r_o - r_{ij}}{B}\right) \qquad \textbf{(1)}$$

The tabulated parameters were obtained experimentally.[30] The r_o parameter depends on the two atoms that form the bond and their oxidation states and B has been take as 0.37 in all the cases, since its variations from one pair of atoms to another is not significant.

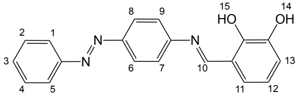
To know the oxidation state of the oxygen was use the BVS equation **(2)**,[31] where **s** represents the oxidation state of the oxygen, **R** is the bond length between the oxygen and an atom and **R**$_1$ and **N** are tabulated parameters.

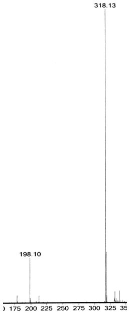
$$s = \left(\frac{R}{R_1}\right)^{-N} \qquad \textbf{(2)}$$

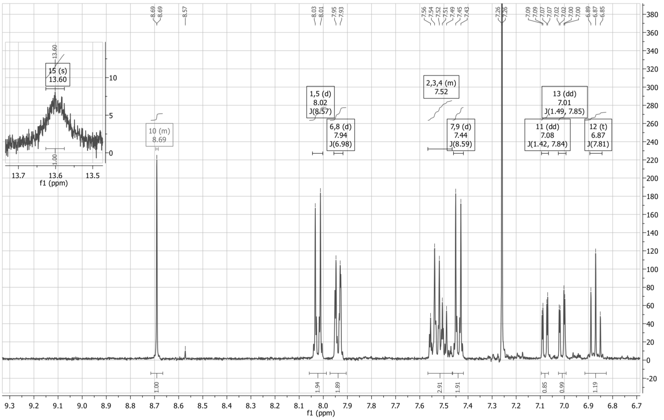
The tabulated parameters were obtained experimentally.[31]

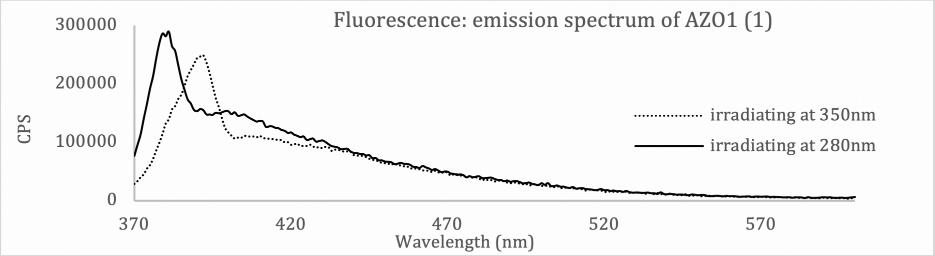
APPENDIX 3: SPECTRA OF THE PRODUCTS: MS, ^{1}H NMR, IR, UV–VISIBLE AND FLUORESCENCE

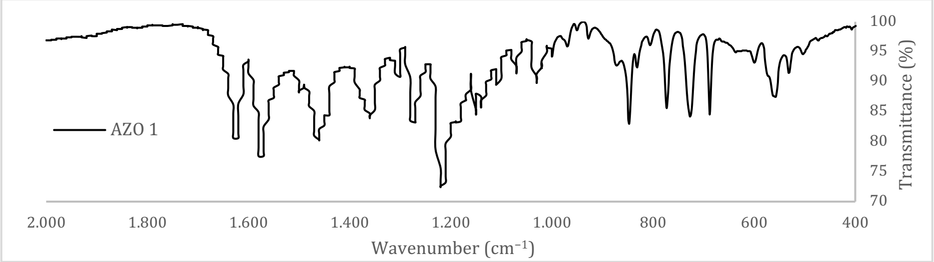
AZO1 (1):

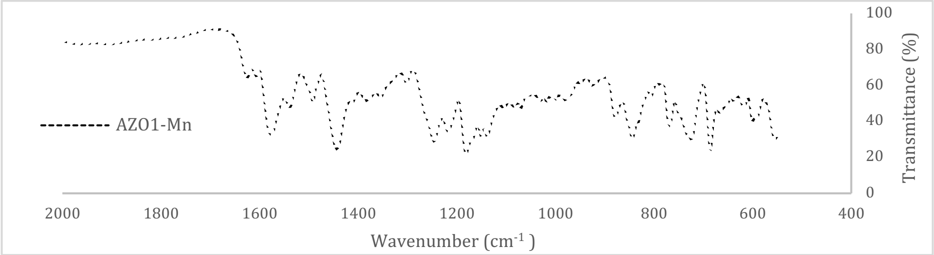




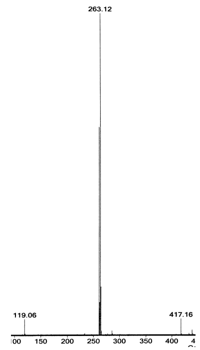


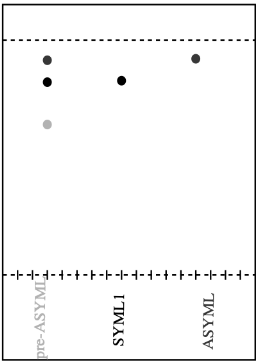




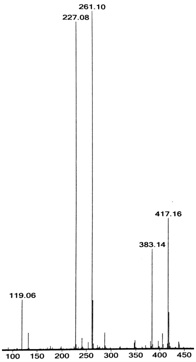


pre–ASYML (2):

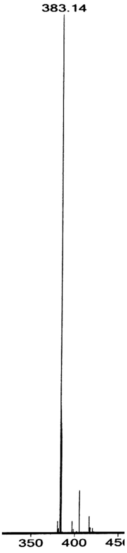


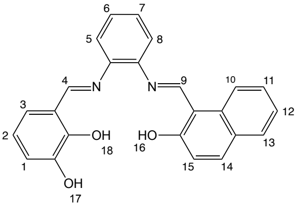


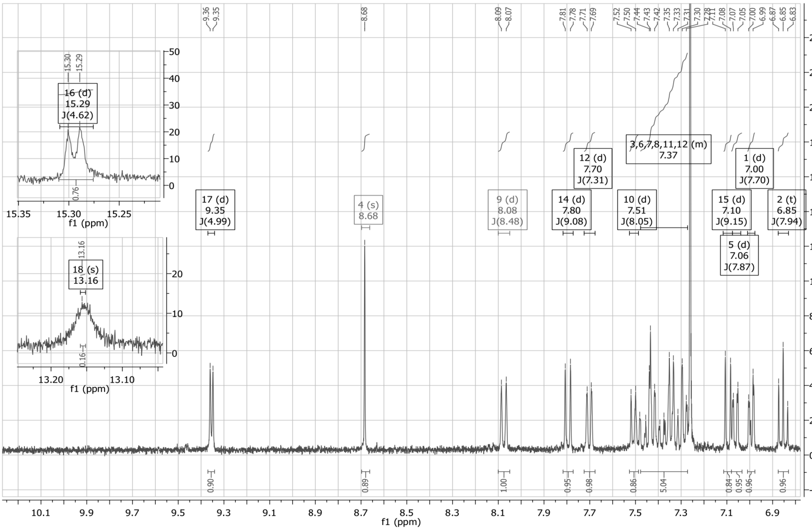
ASYML (3) (method A)

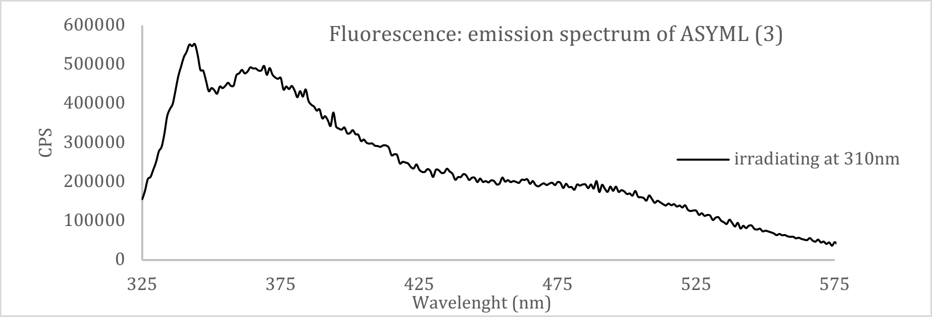


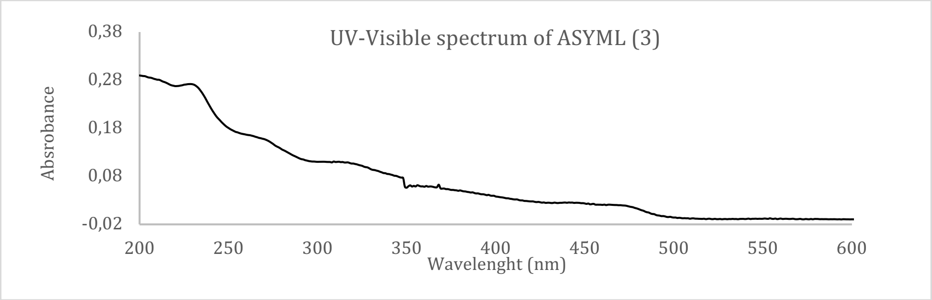
ASYML (3) (method B):

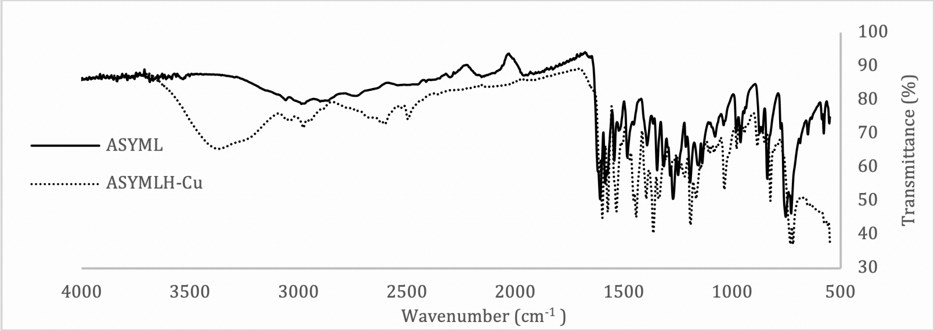


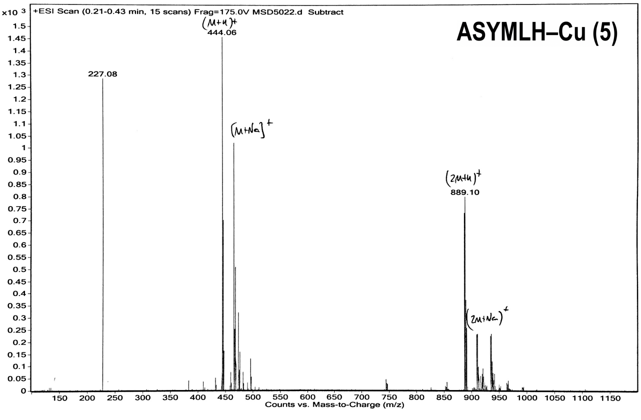




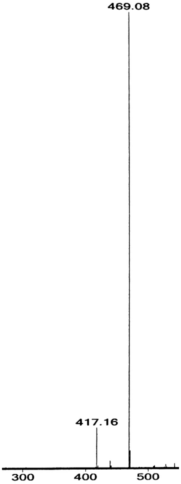

Fluorescence: emission spectrum of ASYML (3)
CPS
600000
500000
400000
300000
200000
100000
0
325
375
425
475
525
575
Wavelenght (nm)
irradiating at 310nm

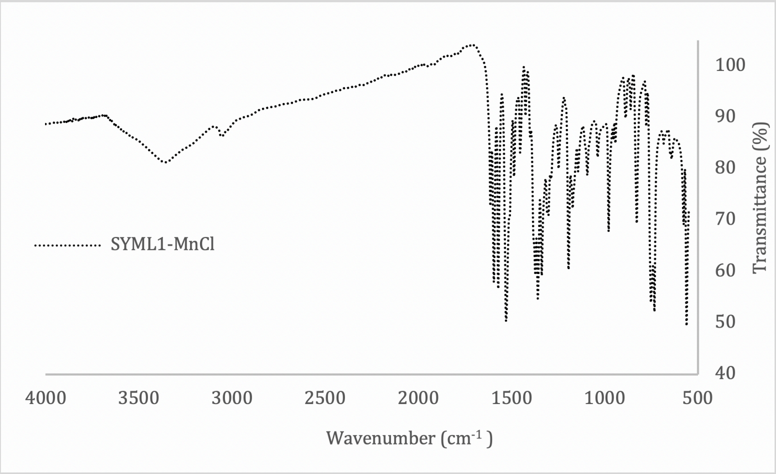

UV-Visible spectrum of ASYML (3)
Absrobance
0,38
0,28
0,18
0,08
-0,02
200
250
300
350
400
450
500
550
600
Wavelenght (nm)


ASYML
ASYMLH-Cu
100
90
80
70
60
50
40
30
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

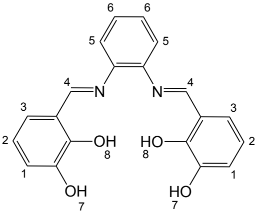

x10 3
+ESI Scan (0.21-0.43 min, 15 scans) Frag=175.0V MSD5022.d Subtract
ASYMLH–Cu (5)
1.5
1.45
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
(M+H)+
444.06
227.08
[M+Na]+
(2M+H)+
889.10
(2M+Na)+
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
Counts vs. Mass-to-Charge (m/z)

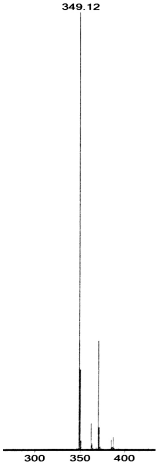
SYML1–MnCl (6):

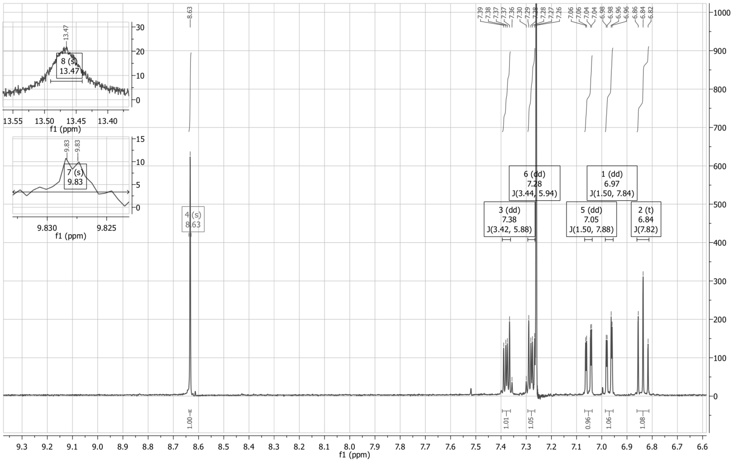


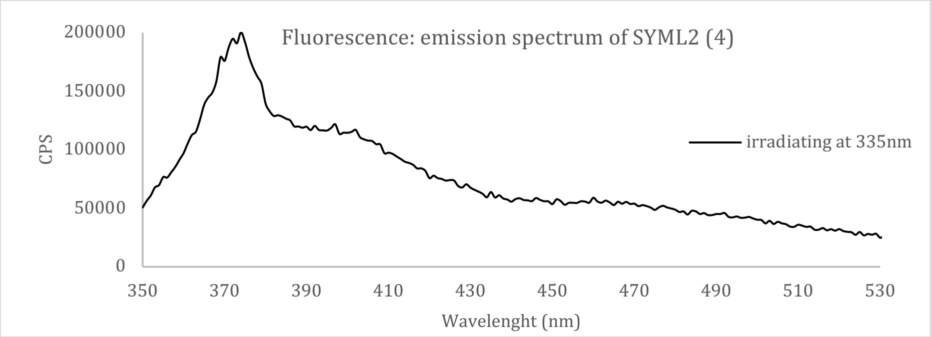


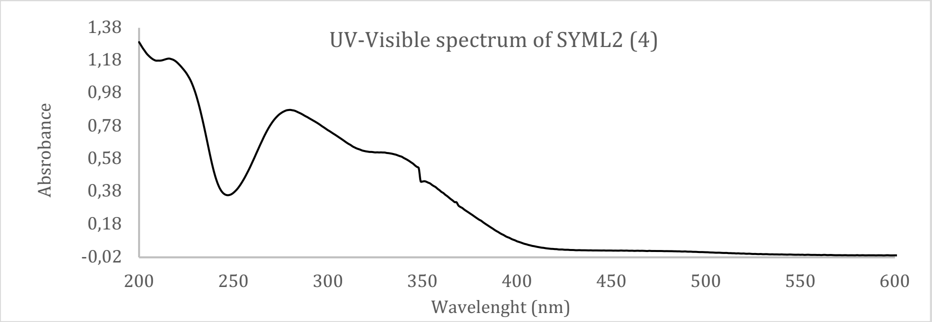
SYML2 (4):

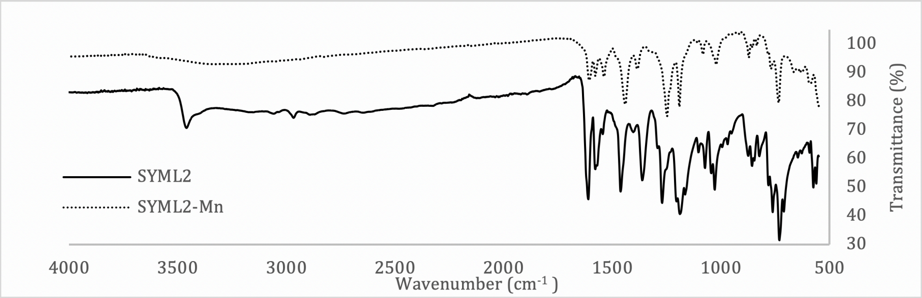


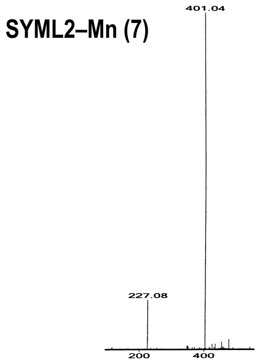





Fluorescence: emission spectrum of SYML2 (4)
CPS
200000
150000
100000
50000
0
350
370
390
410
430
450
470
490
510
530
Wavelenght (nm)
irradiating at 335nm


UV-Visible spectrum of SYML2 (4)
Absrobance
1,38
1,18
0,98
0,78
0,58
0,38
0,18
-0,02
200
250
300
350
400
450
500
550
600
Wavelenght (nm)


SYML2
SYML2-Mn
100
90
80
70
60
50
40
30
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


SYML2–Mn (7)
401.04
227.08
200
400