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BACHELOR THESIS IN CHEMICAL ENGINEERING

Study of cavitand-crosslinked polymers of intrinsic microporosity

Author:
Carlos Grimaldos Lodares
Supervisor:
Prof. Alessandro Pedrini
Co-supervisor:
Dott.ssa Francesca Portone

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ABSTRACT

Microporous materials are solid materials that contain pores with diameters smaller than 2nm. These types of materials are mainly used for gas adsorption and separation, and for heterogeneous catalysis due to their high surface areas of around 300-1500[1] m^2/g^{-1}. Lately, the polymers of intrinsic microporosity (PIM's) have been widely used. These materials are made of soluble organic chains, with a peculiar spatial layout that makes it impossible to pack efficiently, increasing the free volume of the molecule and generating a network of pores with diameters below 2 nm. In this thesis, the aim was to synthetize PIM-1 and PIM-1 with AC-TetraOH QxCav$_1$ inside it. This have been done in order to study the effects that including a quinoxaline cavitand in the polymer can have on mechanical and gas separation properties of this polymers.

Regarding the synthesis of the crosslinked PIM-1, an AC-tetraOH QxCav$_1$ was initially synthesized bearing four hydroxyl groups on the quinoxaline walls in A-C positions. This cavitand will be used to be inserted in the polymer for the subsequent synthesis of the functionalized PIM-1 (**Scheme 1**). During the synthesis process made up of four steps, the last one was problematic and gave no product, so finally an OctaOH QxCav$_1$ pre-synthetized by our work-group was used.

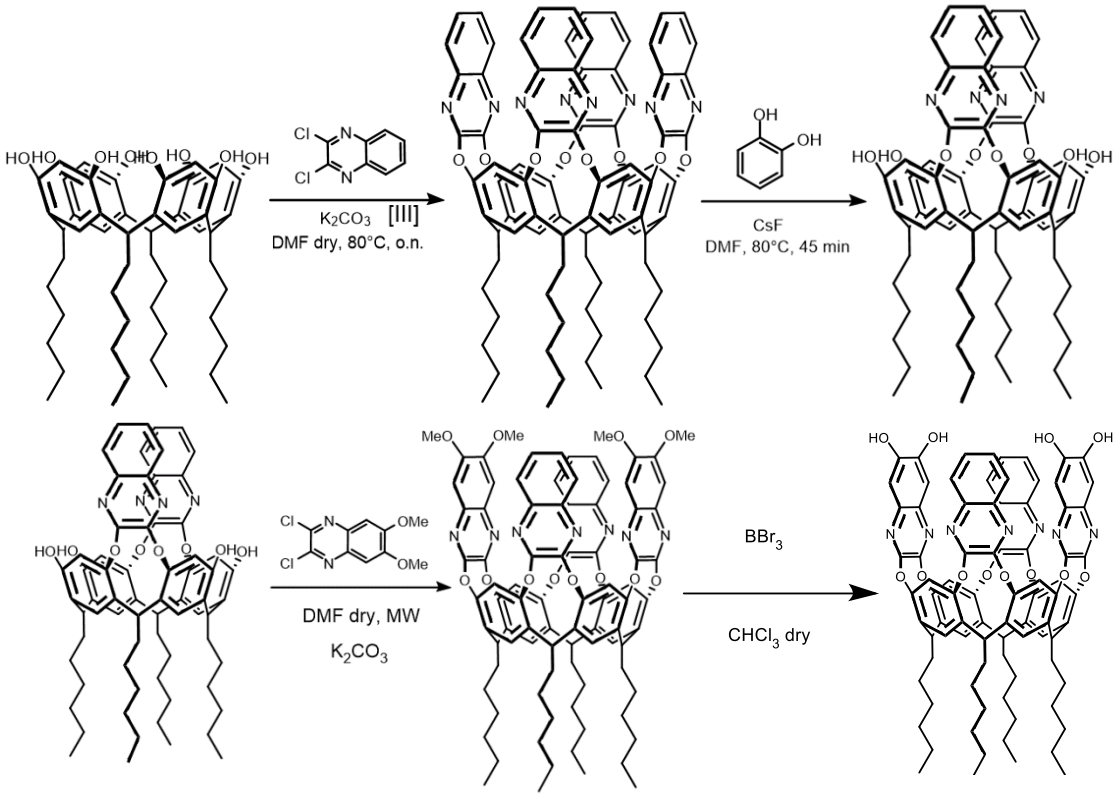
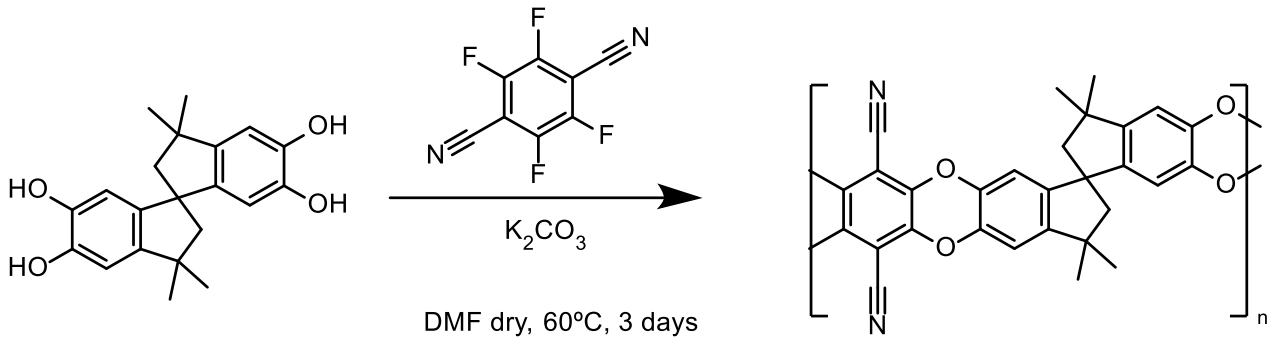


Figure 1: Synthesis of the AC-TetraOH QxCav$_1$ used.

Consecutively, the PIM-1 was synthetized following the procedure exposed in the literature as low temperature synthesis[1]. The product was then characterized by ^{1}H-NMR spectroscopy and infrared spectroscopy (IR).



Scheme 1: Synthesis reaction scheme of the PIM-1.

The last part of the thesis was dedicated to the preparation of PIM-1 films by slow evaporation of the solvent. Thin and homogeneous films of PIM-1 were obtained starting from a 3% w/w solution of PIM-1 in chloroform (**Figure 2**). It was also possible to obtain a crosslinked PIM-1 film using a mixture of a PIM-1 and crosslinked (with octaOH quinoxaline cavitand) PIM-1 (15% w/w) using a blending approach[2]. Then, same as for PIM-1 slow evaporation of the solvent was used to obtain the film.

Figure 2: Photo of the PIM-1 film (left) and the crosslinked PIM-1 (right) films obtained.

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INTRODUCTION

Microporous materials

Microporous materials are materials containing pores with diameters below 2nm. Some classical examples of microporous materials (and the most used) are zeolites (aluminosilicates) and activated carbons. These type of materials are mainly used for adsorption (for example, in industry with highly pollutant emissions, adsorption is one of the best options to reduce the pollutant concentration in the final outgoing emission and so industries can abide by environmental laws) and for heterogeneous catalysis due to their high surface areas of around 300-1500[1] m^2 g^{-1}. In literature are known several examples of microporous materials such as zeolites[3], Metal Organic Frameworks (MOFs)[3] and other. Lately a new type of microporous materials is appearing, the Polymers of Intrinsic Microporosity (PIMs). These materials are made of soluble organic chains, which along crosslinking mechanisms for the polymer chains leads to the possibility of the formation of polymeric membranes capable to act as a microporous adsorbent.

PIMs (Polymers of Intrinsic Microporosity)

The polymers of intrinsic microporosity (PIM) were firstly developed by Peter Budd and Neil McKeown in the first decade of the 2000's[1]. PIMs are classified as microporous materials due to the contorted and rigid chains that are not able to pack efficiently, generating a network of intermolecular voids with a width under 2nm. The microporosity of PIMs is *intrinsic* because it arises only from their molecular structure (**Figure 3**) and it is not dependent on the thermal or processing history of the material; this means that the surface area of a recently synthetized and precipitated PIM will be the same as samples that have been exposed for long-lasting periods of time under ambient conditions or heated at high temperatures (under decomposition temperatures) [3]. These properties give them a high thermal stability, which can be confirmed also with no presence of glass transitions or melting point below the decomposition temperature, about 370 °C[1].

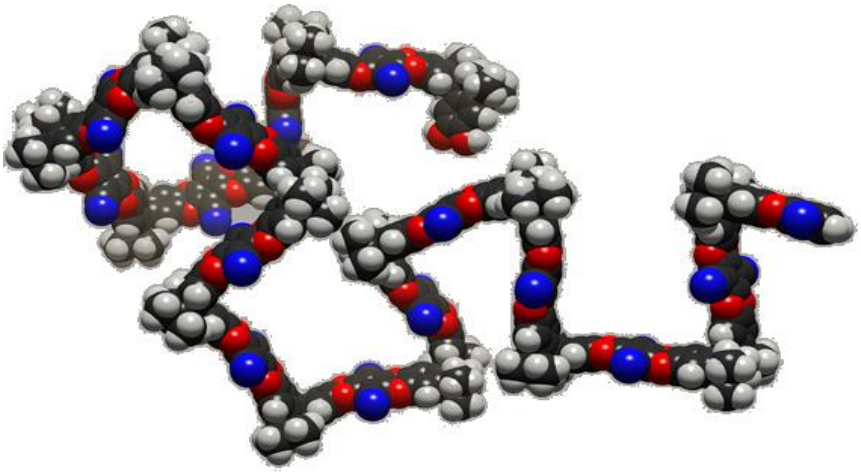


Figure 3: 3D spatial structure of PIM[1].

These polymers are made by double nucleophilic aromatic substitution (**figure 4**). One of the monomers is an aromatic tetra-alcohol while the other one is a fluoro derivate molecule. These reactions are favoured in the presence of electro-withdrawing groups (ie -CN, -F). Due to their reactive tetrol units and nonlinear shape, the necessary sites of contortion are introduced into the resulting PIM[1].

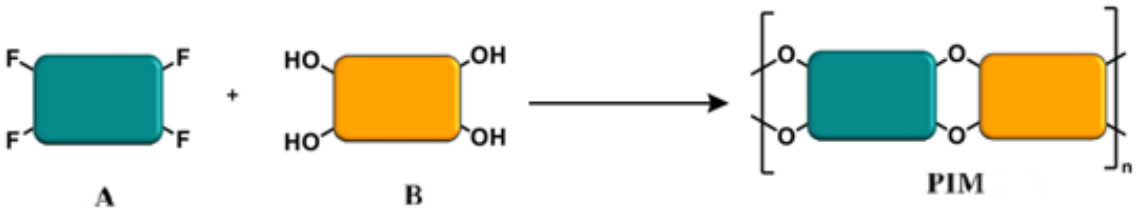


Figure 4: General synthesis of PIMs.

In this project is exploited only PIM-1, the most famous, shown in **Scheme 2.** It should be noted that there are many different PIMs depending on their monomers. In general it is possible to see different combinations of monomers for the synthesis of PIMs (**Figure 5**[1]), always following the general reaction showed in **Figure 4**. The thread of the synthesis is the presence of rigid structures that lead to a contortion site (A1), or via a single covalent bond that prevents rotation (A2 and B2) and allow the formation of a microporous network.

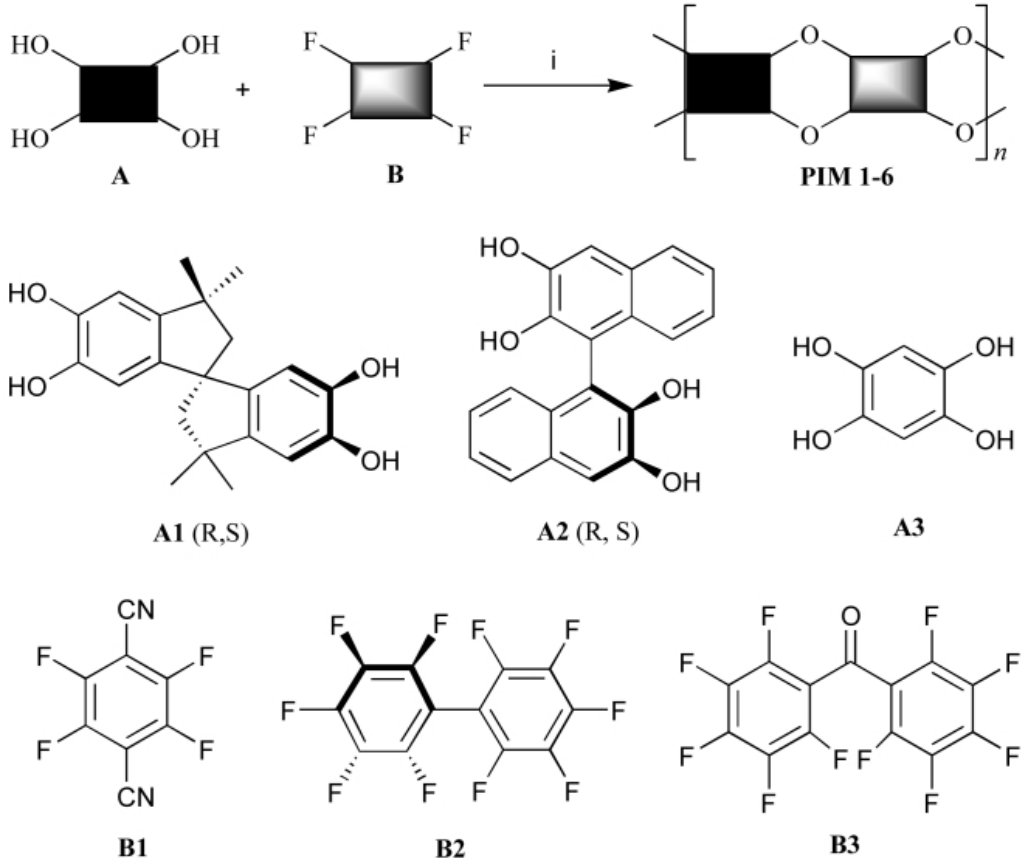
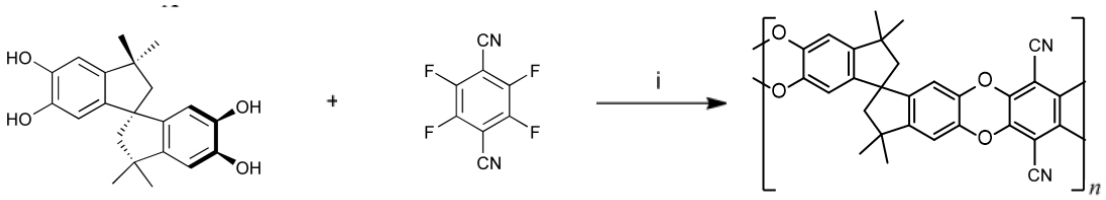


Figure 5: Different combinations of monomers used in the synthesis of PIMs.

PIM-1 monomers are 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (A1) and 2,3,5,6-tetrafluoroterephthale-nitrile[4](B1), both commercially available.

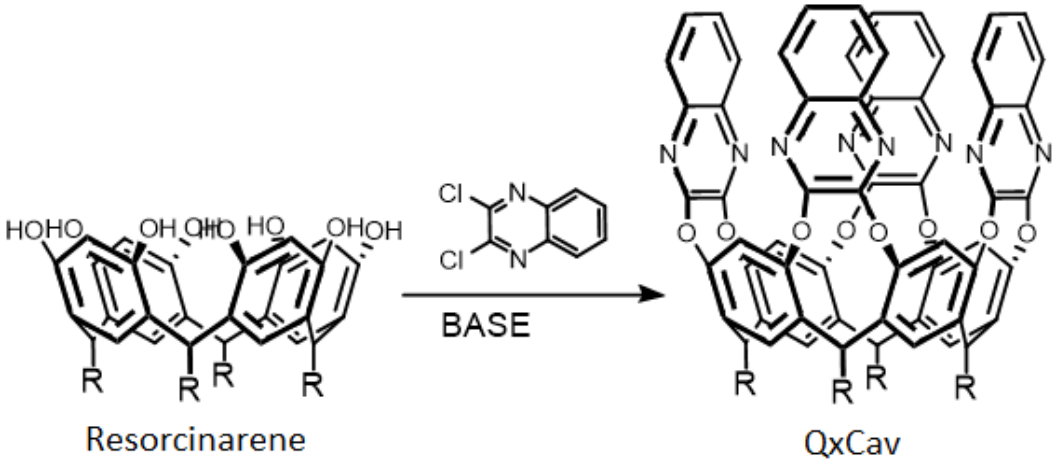


Scheme 2: Synthesis scheme of PIM-1.

A limitation of PIMs that prevents their use for applications such as membranes is due to the phenomenon of ageing and plasticization, which leads to the loss of their permeability over time. One strategy to avoid these phenomena consists in reinforcing the microstructure of the polymer by adding a cross-linking agent. For this purpose, in this thesis the use of a quinoxaline cavitand as the cross-linking agent is proposed. Furthermore, this addition of the cavitand can lead to additional benefits such as increased adsorption properties[5].

Quinoxaline cavitands

Quinoxaline cavitands are resorcinarene based macrocyclic molecules made from the result of a bridging reaction of a resorcinarene with a quinoxaline (**Scheme 3**). The quinoxaline molecule can be functionalized according to the wanted properties. This special structure makes a cavity that allows the molecule to practice host-guest chemistry using guest molecules of complementary shape and size [6].



Scheme 3: Synthesis scheme of a quinoxaline cavitand.

A peculiarity of this type of molecules is their ability to interconvert reversibly from a closed conformation called “vase” to an open one called “kite”, as reported in **Figure 6**.

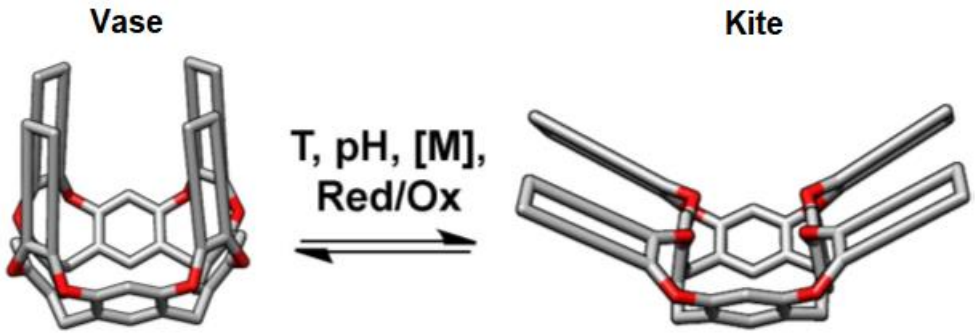


Figure 6. Interconversion of a generic quinoxaline cavitand between the vase and kite conformation[7].

The switching between the two conformations can be reversibly induced by various external stimuli, such as temperature, Redox or the pH[3]. Considering the latter, the kite form is favoured at low pH values as the protonation of the nitrogen atoms of the quinoxaline generates an electrostatic repulsion between the neighbour amino groups, causing the opening of the quinoxaline walls. Recently, our research groups, demonstrated that when quinoxaline cavitands are embedded into a polymeric matrix, the switching between these two conformations can be triggered by mechanical stress (**Figure 7**)[2].

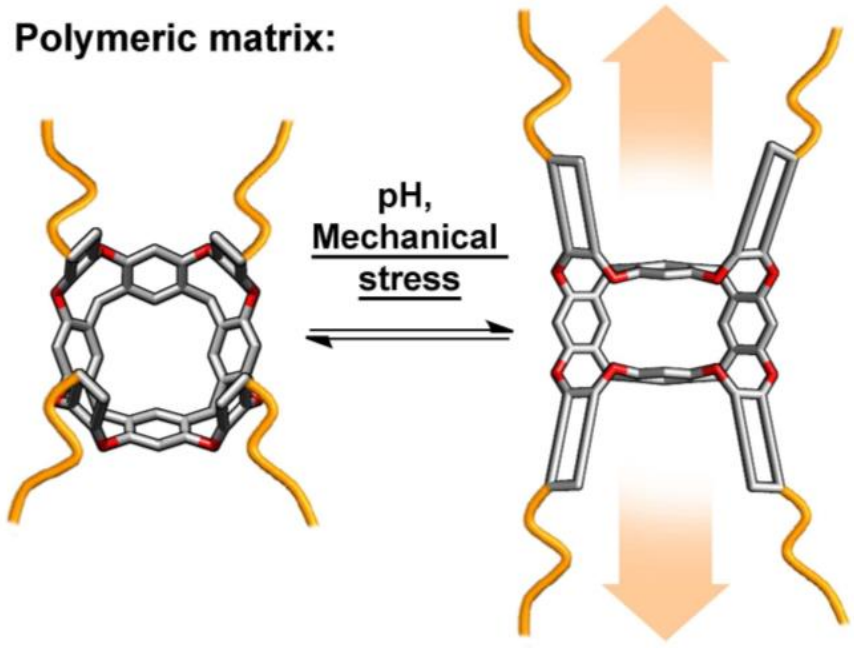


Figure 7: Opening of a quinoxaline cavitand in a polymeric matrix.

In this project, the quinoxaline cavitand is functionalized in the top part with -OH groups but only in AC positions. The goal is to produce a PIM-1 with the cavitand showed in **Figure 8** inside the network.

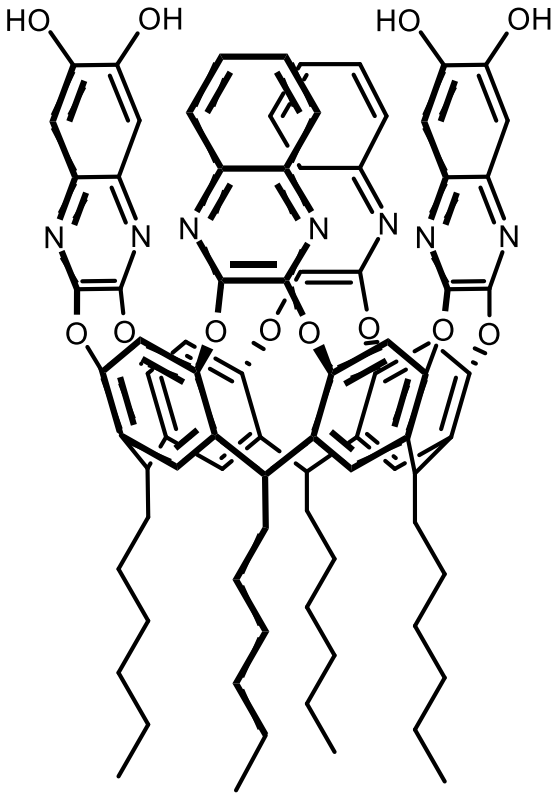


Figure 8: tetra OH QxCav synthetized in this project

Anyway, in this project, an octaOH QxCav, which was previously synthetized by another laboratory student, as well as the PIM-1 obtained using this cavitand as crosslinker (**Figure 9**) have been used. This crosslinked PIM-1 was finally casted into a film during the course of this project.

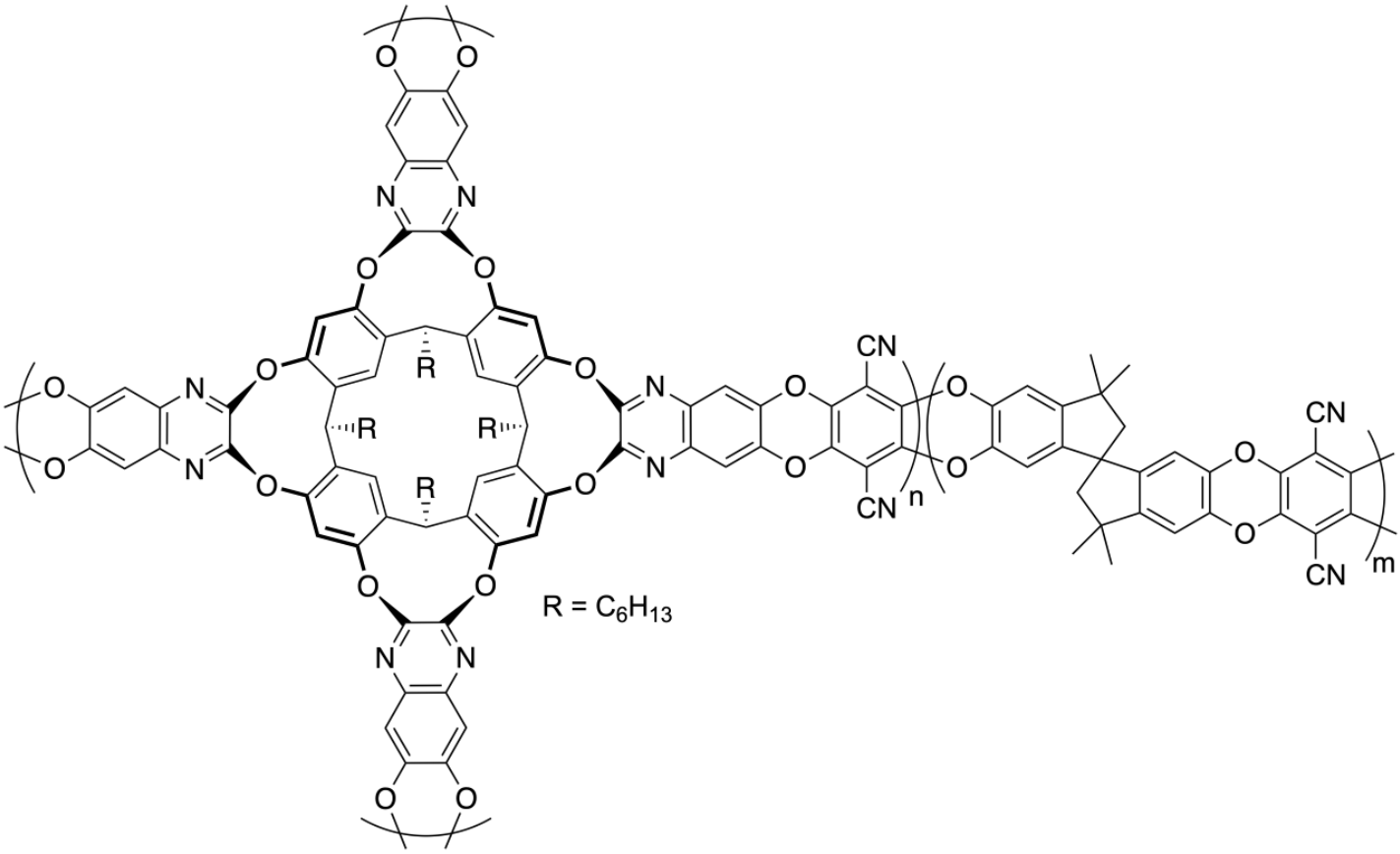


Figure 9: Structure of the crosslinked PIM-1 previously synthetized.

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RESULTS AND DISCUSSION

The main scope of this project is the study and development of polymers of intrinsic microporosity (PIMs) using quinoxaline cavitands as comonomers and cross-linkers.

The project is divided in three main parts:

1. Synthesis of the polymer of intrinsic microporosity used (PIM-1).

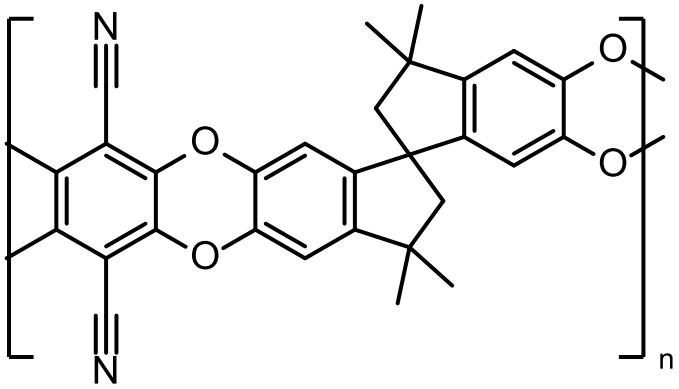


Figure 10: Molecular structure of PIM-1.

2. Synthesis of the AC-TetraOH QxCav$_1$ and making of PIM-1 film and cavitand-functionalized PIM-1 film using OctaOH QxCav$_1$:

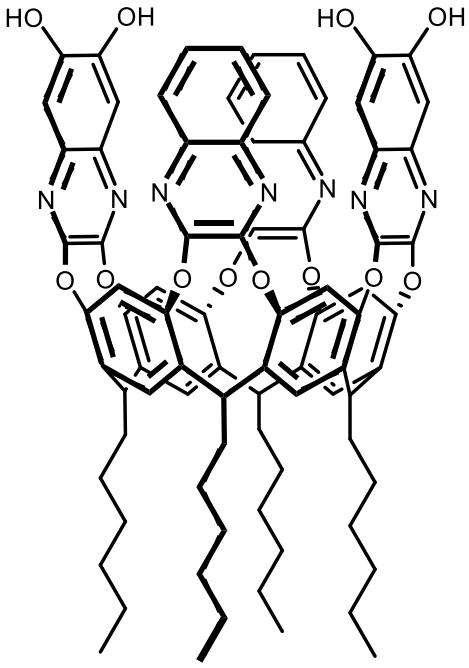
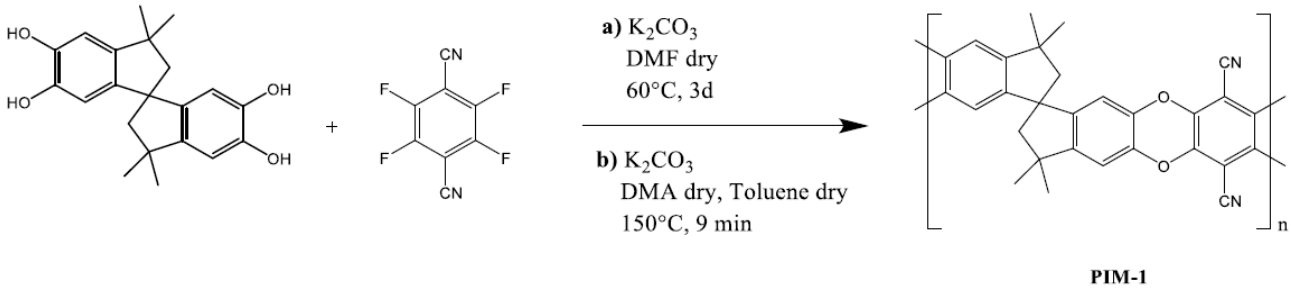


Figure 11: Molecular structure of AC-tetraOH QxCav.

2.1 Synthesis of the polymer (PIM-1).

Following the literature [5] there are two main procedures for the synthesis of the PIM-1, the high-temperature (HT) and the low-temperature (LT) method as schematize in **Scheme 4**.

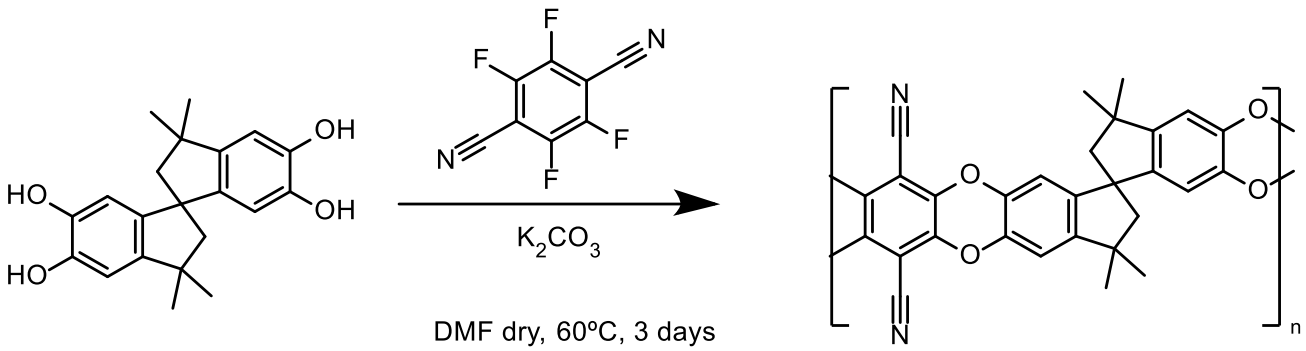


Scheme 4: Scheme of low-temperature (a) and high-temperature (b) method for PIM-1 synthesis.

In this project, it was used the low-temperature method since previous study was performed in our group showing a better distribution of molecular weight of the final polymer even if the method chosen is slower in terms of time.

The monomers for the achievement of PIM-1 were 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane and 2,3,5,6-tetrafluoroterephthale-nitrile. The reaction is an aromatic nucleophilic substitution, the electron attracting nature of the nitrile and fluorine groups favoured the substitution.

The reaction was carried out at 60°C for 3 days using K_2CO_3 as base to help deprotonate the OH group of the monomer. This reacting was made using DMF dry as solvent and lead to the formation of benzodioxane linker (**Scheme 5**).



Scheme 5: Synthesis scheme of PIM-1 at low temperature.

The crude obtained was then precipitated in water, filtered, reprecipitated in methanol and finally placed in water reflux for two hours to remove the salts formed during the reaction (KF and excess of K_2CO_3).

Finally the product was characterized by ^{1}H-NMR spectroscopy (**Figure 12**) and IR spectroscopy (**Figure 13**).

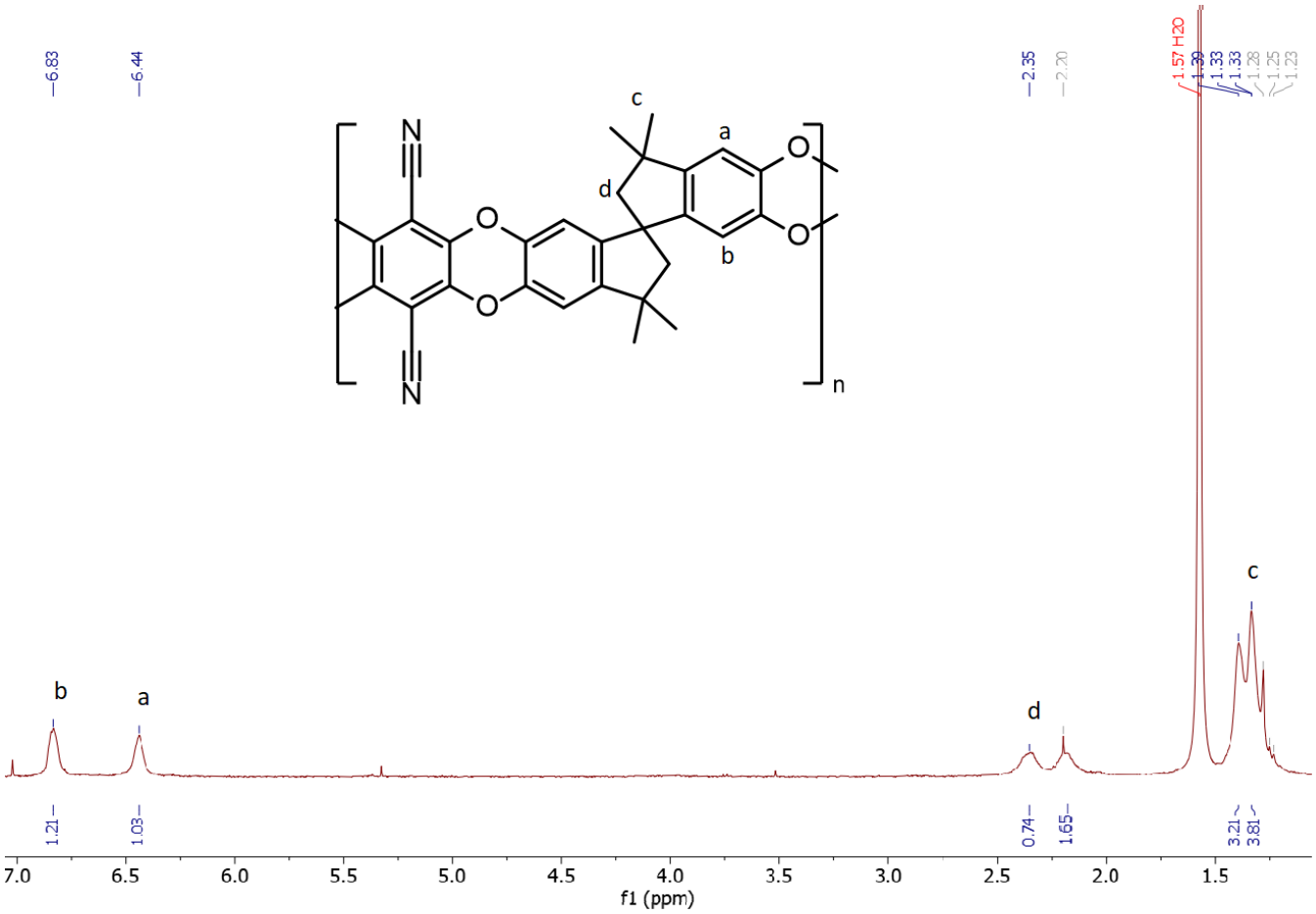


Figure 12: ^{1}H-NMR spectrum ($CDCL_3$, 400MHz) of the PIM-1.

In the ^{1}H-NMR spectrum it is possible to notice, in the aromatic region, two singlets related to the two aromatic protons H_b (6.83 ppm) and H_a (6.44 ppm). At 2.35 ppm and 2.20 ppm are shown the signal of the CH_2 (H_d), it is a doublet because the two hydrogens atoms are placed on different planes with respect to the one of the molecule.

Finally, at 1.39-1.33 ppm there are the signals of the methyl groups on the spiroindane moiety. The spectrum obtained is coherent when comparing with the one reported on literature.

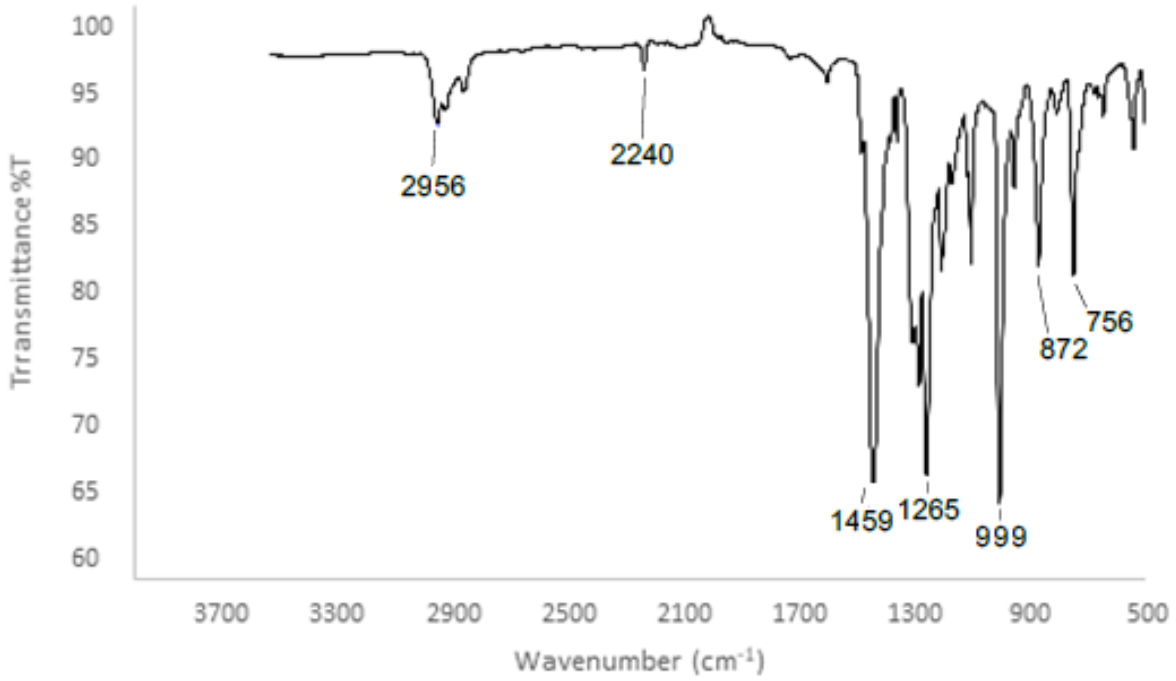


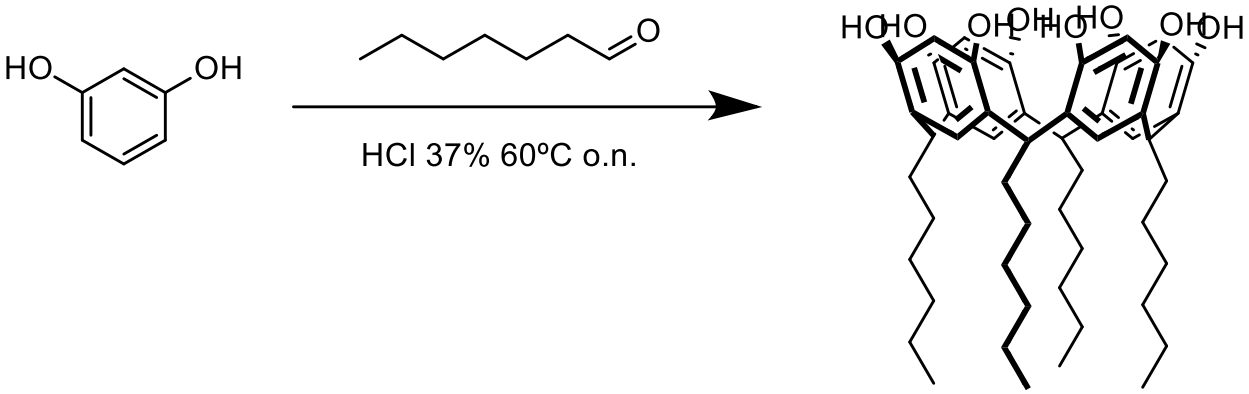
Figure 13: IR spectrum of the PIM-1 syntethyzed.

From the IR spectrum it is possible to observe the presence of a signal at 2240 cm^{-1}, characteristic of stretching of the nitrile group. Furthermore, at 2956cm^{-1} are visible the signals relating to the stretching of aromatic and aliphatic C-H.

2.2 AC-tetraOH QxCav$_1$ synthesis

Synthesis of Res[C_6,H_{13},H]

For the synthesis of the desired cavitand, the first step is the synthesis of the resorcinarene (**Res[C_6,H_{13},H]**) starting from resorcinol and heptanaldehyde. Resorcinarenes are macro-cyclic molecules product of the condensation of resorcinol and an aldehyde in an acidic medium[5]; this aldehyde defines the functionalization at the lower rim of the molecule.



Scheme 6: Reaction scheme of **Res[C_6,H_{13},H]** synthesis.

The reaction took place at 60°C for 16 hours using methanol and HCl_{aq} 37% as solvents. This latter will act both as solvent for the reaction and catalyst. The pure product was obtained via recrystallization in methanol with a yield of 49%.

The product was characterized by ^{1}H-NMR spectroscopy (**Figure 14**).

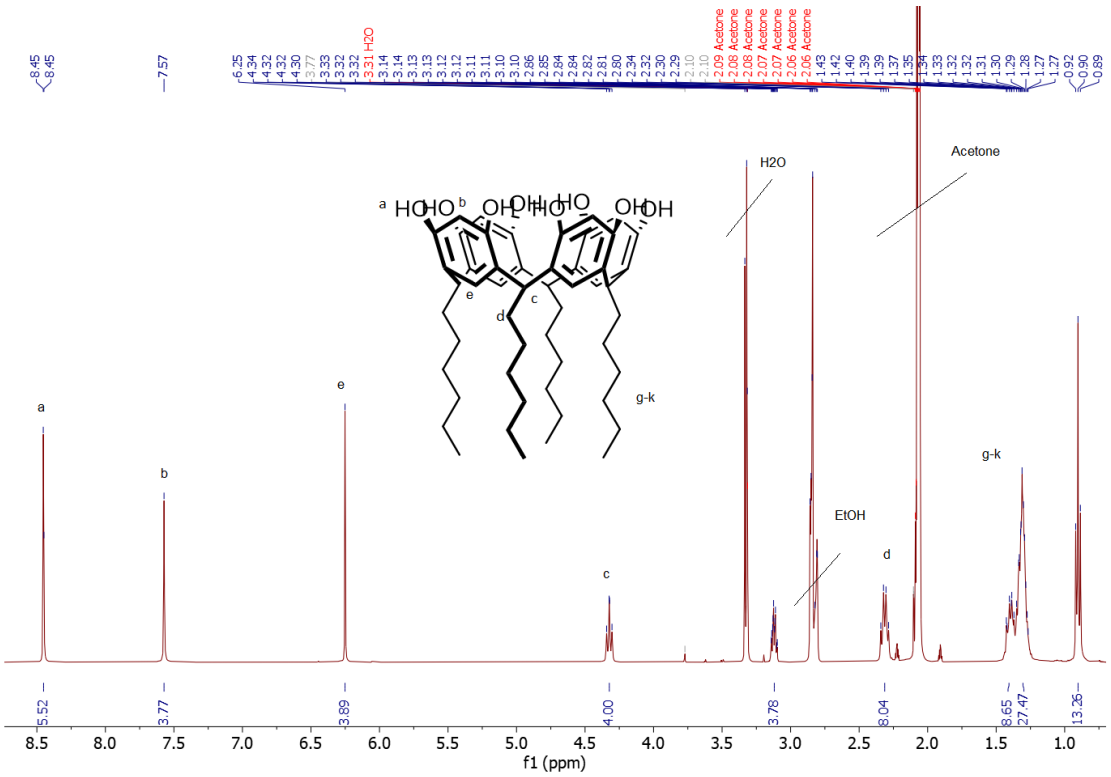
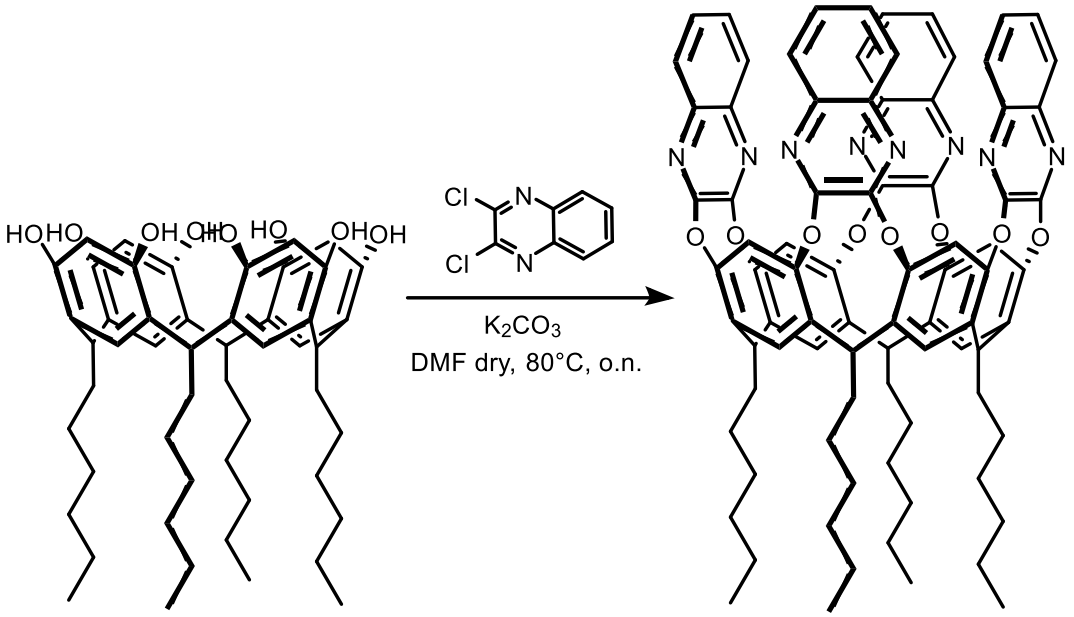


Figure 14: ^{1}H-NMR spectrum (acetone-d_6, 400MHz) of **Res[C_6,H_{13},H]**.

As seen in the spectrum it is possible to identify the phenolic protons (8.45 ppm) and the aromatic protons H_b (7.57 ppm) and H_e (6.25 ppm) in the aromatic region. It is also visible the diagnostic triplet of the bridging protons at 4.32ppm.

Once this step has been done, then follow the bridging reaction between the 2,3-dicloro-quinoxaline on **Res[C_6,H_{13},H]** as reported in **Scheme 7:**



Scheme 7: Scheme of the reaction for the synthesis of the $QxCav_1$.

The reaction was performed in anhydrous environment¡, in presence of K_2CO_3 as base and using DMF dry as solvent. The reaction went at 80°C for 16 hours. The product was purified from the partial bridging by-products via recrystallization in ethyl acetate. The product, which appears as a white solid, is finally characterized by ^{1}H-NMR spectroscopy (**Figure 15**).

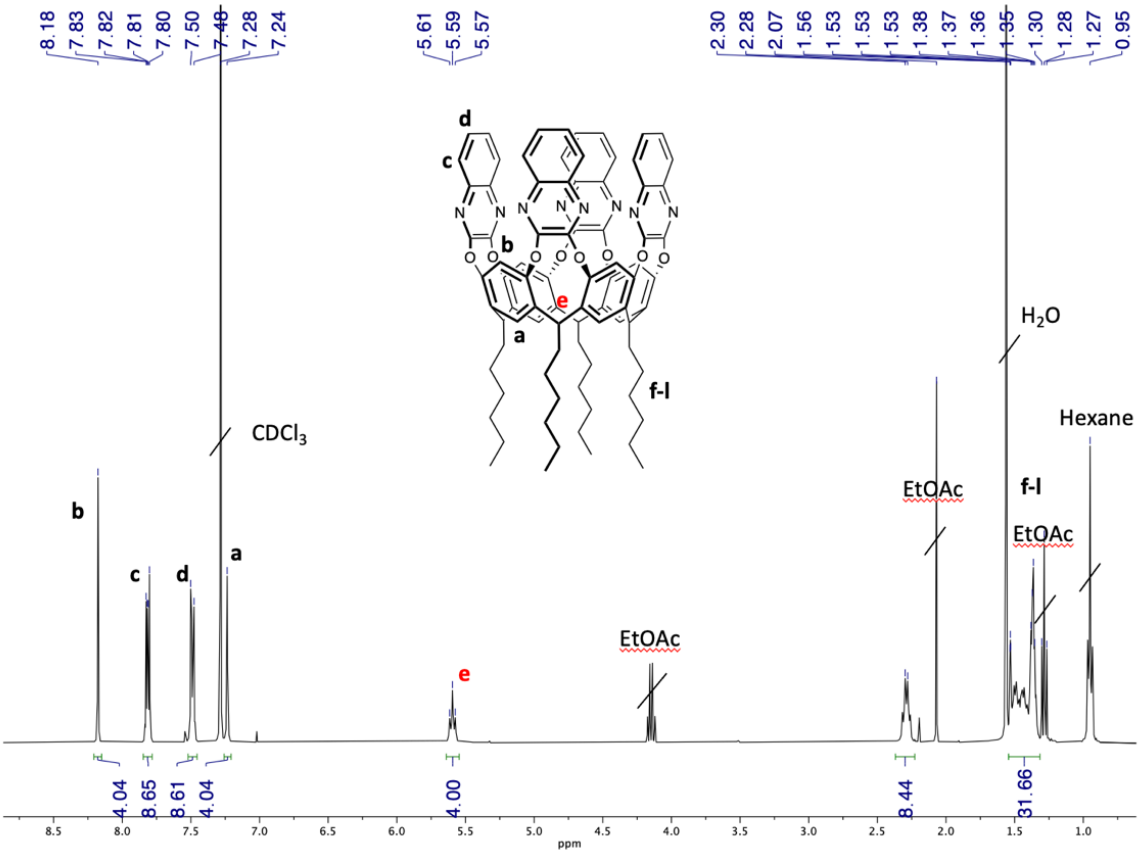
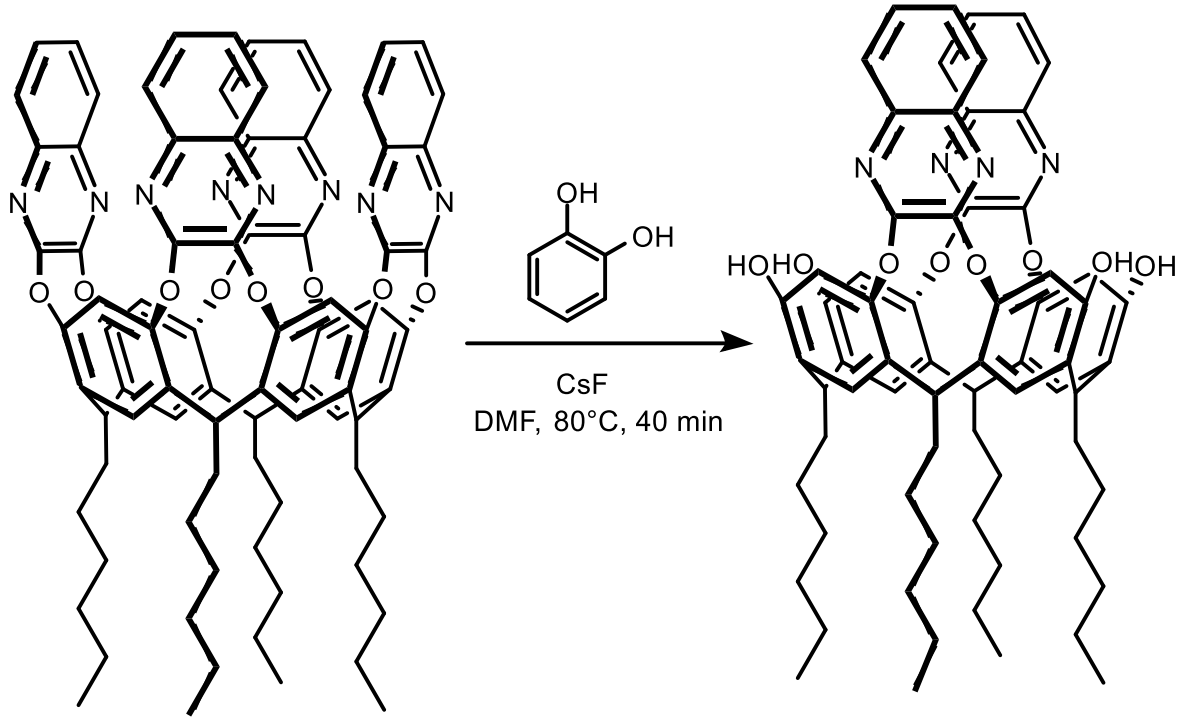


Figure 15: ^{1}H-NMR spectrum ($CDCL_3$, 400MHz) of the $QxCav_1$.

In the ^{1}H-NMR spectrum is visible at 5.59 ppm (H_e) a triplet corresponding to the bridging protons of the molecule. It is also possible to identify the protons of the quinoxaline H_c and H_d at 7.82 ppm and 7.49 ppm respectively. Finally the phenolic protons are also visible at looking in the aromatic region, 8.18 ppm (H_b) and 7.24 ppm (H_a).

Synthesis of AC-tetraOH-QxCav.

The next step was the excision reaction of the $QxCav_1$ previously synthetized. In this reaction catechol offers two appropriately spaced oxygen atoms to efficiently attack the quinoxaline moiety[8]. The wanted product is only the AC-$QxCav_1$ so after the reaction is finished there will be other isomers of the molecule that needed to be separated.



Scheme 8: Reaction scheme of the synthesis of the AC-QxCav.

The reaction was made by slowly adding cathecol to a solution of the $QxCav_1$ in DMF in presence of CsF as base. The reaction went for 40 minutes at 80°C and after a precipitation in iced brine, the crude obtained is purified by column chromatography (DCM/EtOAc 95/5 ⇨ 85/15). Finally the product is obtained and characterized by ^{1}H-NMR spectrum (**Figure 16**).

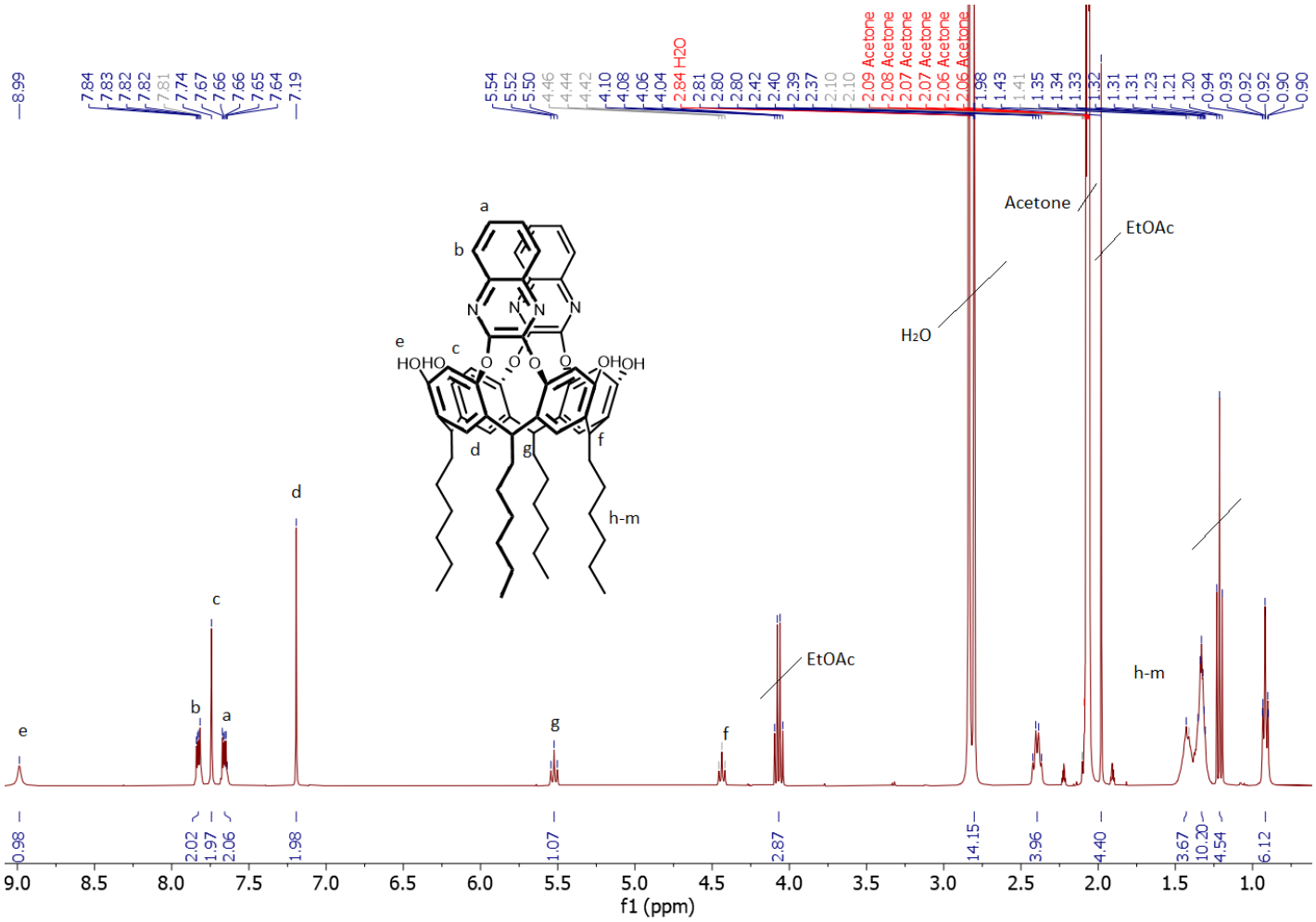
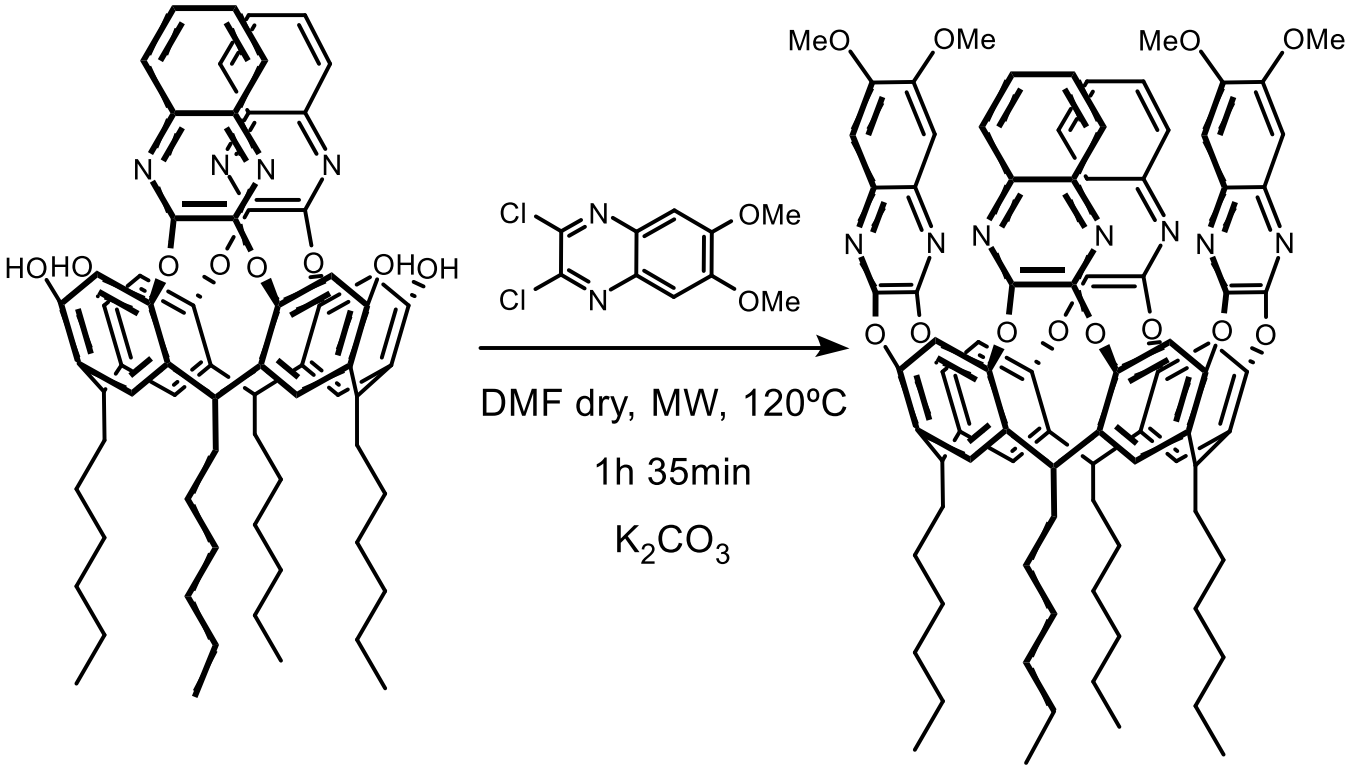


Figure 16: ^{1}H-NMR spectrum (acetone-d_6, 400MHz) of the AC-QxCav$_1$.

In the ^{1}H-NMR spectrum it is possible to see, in the aromatic zone, the aromatic proton signals of quinoxaline, H_b at 7.82 ppm and H_a at 7.65 ppm, as well as the signals of the resorcinarene, H_c at 7.74 ppm and H_d at 7.19 ppm. The protons from the -OH groups can be seen at 8.99 ppm (e). A peculiarity is the presence of H_g and H_f at 5.55 ppm and 4.44 ppm respectively, two triplets relatives the bridging protons of the cavitand. These two different peaks confirm that the reaction has been done successfully and that the quinoxalines are only present in AC sites.

The next step was the bridging reaction, with 2,3-dichloro-6,7-dimethoxy, bearing two -OMe protective groups on the AC-QxCav$_1$.



Scheme 9: Reaction scheme of the synthesis of the AC-OMe $QxCav_1$.

The reaction was performed in DMF dry in microwave for 1.35 hours with the presence of K_2CO_3 as base. The 2,3-dichloro-6,7-dimethoxy quinoxaline was previously synthetized in the research group. At the end of the reaction, the solvent was removed by vacuum trap and the dry crude was then purified from the by-products of partial bridging reactions, by column chromatography (DCM/EtOAc 95/5). Finally, the product is characterized by ^{1}H-NMR spectroscopy (**Figure 17**).

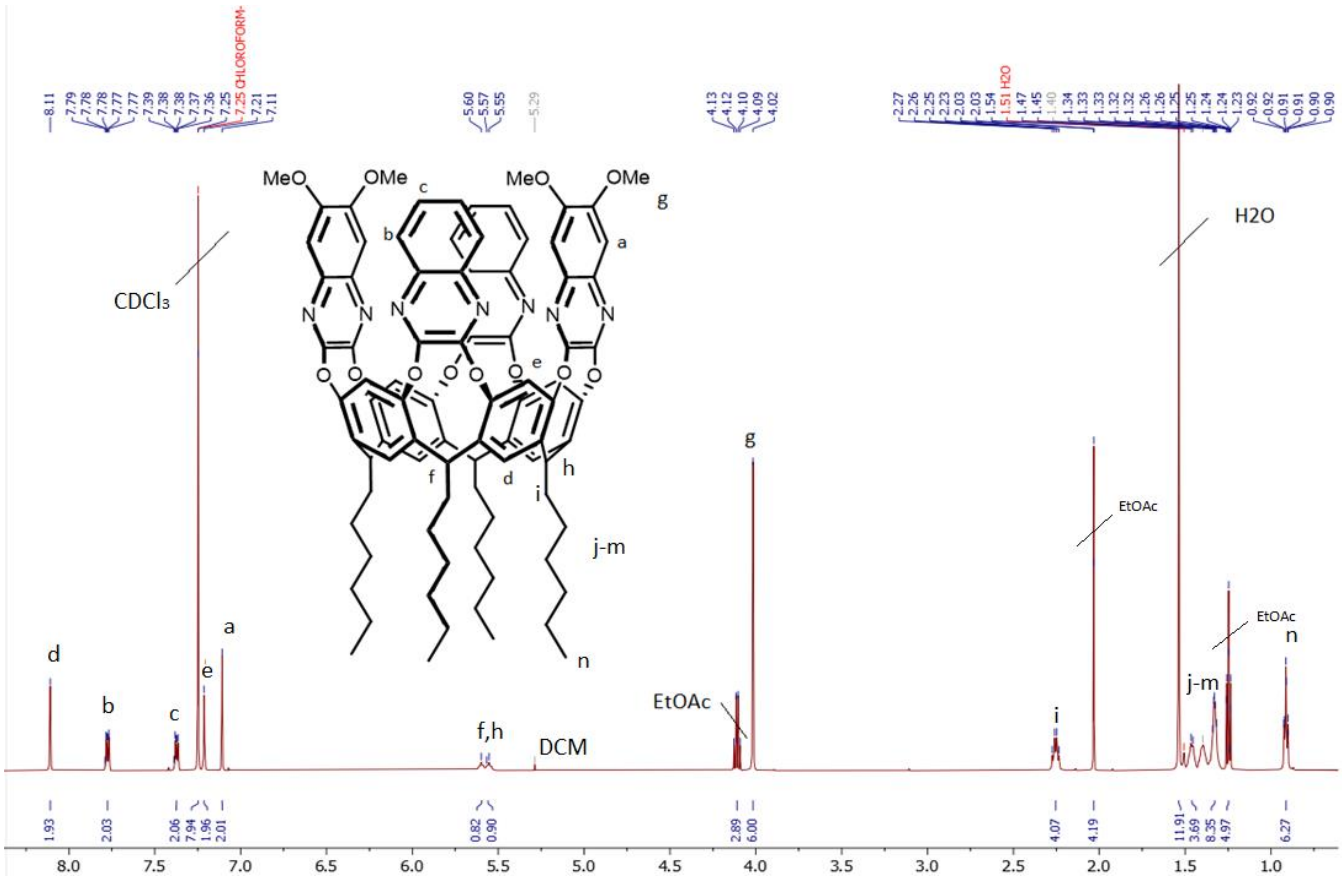
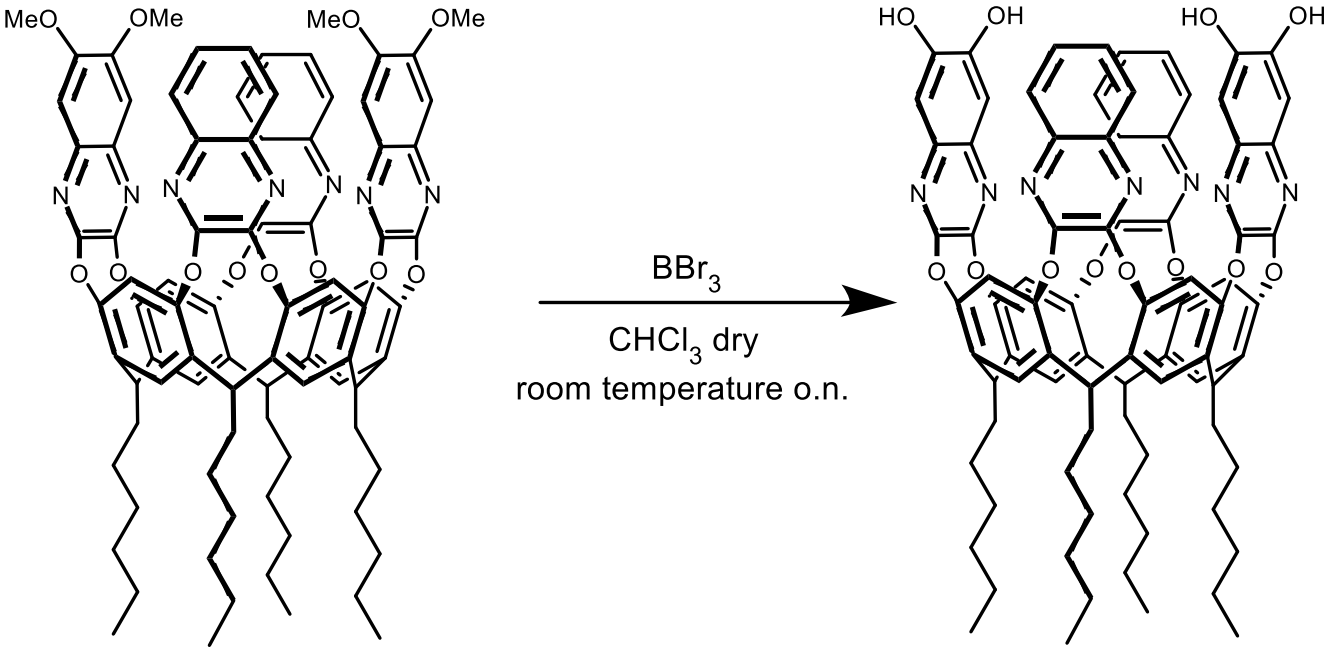


Figure 17: ^{1}H-NMR spectrum ($CDCL_3$, 600MHz) of the AC -OMe $QxCav_1$.

In the ^{1}H-NMR spectrum it is possible to see two different peaks at 5.6ppm (f) and at 5.56 ppm (h) given by the bridging protons; this still confirms the presence of the AC functionalization. The difference between these peaks is small because the only difference between the protons coupling is the -OMe group on the quinoxaline. In the aromatic zone, is possible to see both protons from the quinoxaline without the -OMe group at 7.78 ppm (H_b) and 7.38 ppm (H_c), aswell as the aromatic protons form the protected quinoxaline with the -OMe at 7.11 ppm (H_a). Considering everything, it is possible to confirm that the characterized product is the wanted one and the reaction has been made successfully. MALDI-TOF analysis also highlights the purity of the product.

Finally, the last step in the obtaining of the tetra OH-$QxCav_1$ is the deprotection of the methoxy moieties of the AC -OMe $QxCav_1$.



Scheme 10: Reaction scheme of the synthesis of the AC-tetraOH QxCav$_1$.

The reaction was made by carefully adding BBr_3 to a solution of the protected AC -OMe QxCav$_1$ in $CHCl_3$ under anhydrous conditions, as BBr_3 is highly reactive with the water present in the humidity of air. BBr_3 is a strong Lewis acid that can deprotect the methoxy groups present at the upper rim of the cavitand[6]. The reaction was stirred for 16 hours at room temperature. The solvent was then remove via vacuum trap

The crude product was then analysed via MALDI-TOF spectrometry (**Figure 18)** that shown the presence of traces of product. Further purification with column chromatography was carried out but no results was observed. It can be probably for a partial degradation of the product since in TLC the spot of the reagent was not present anymore.

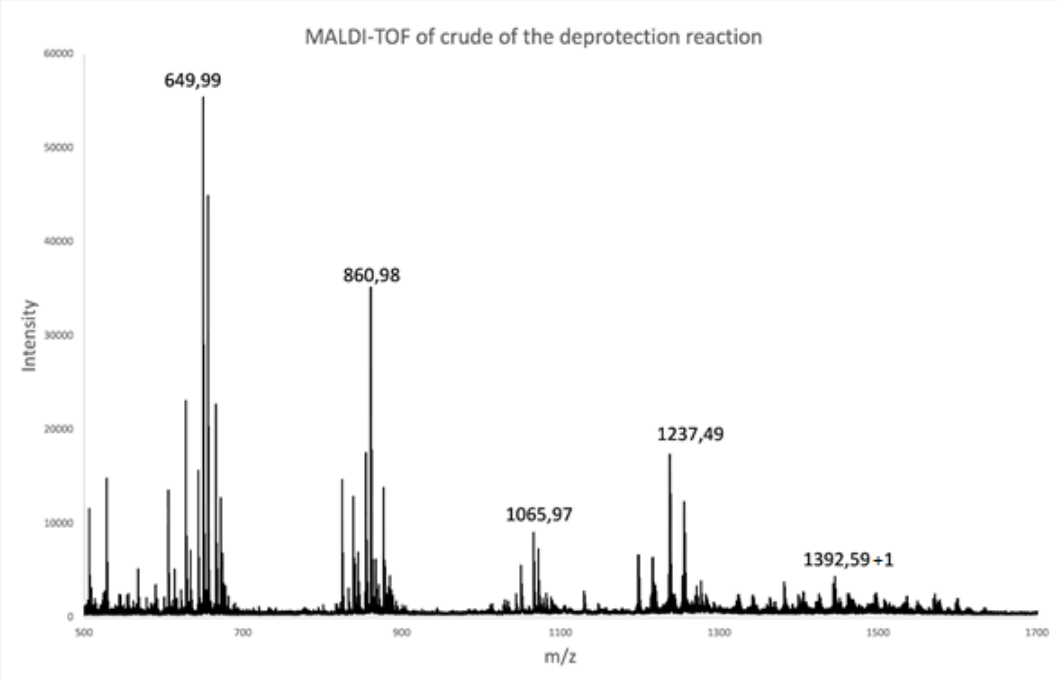


Figure 18: MALDI TOF spectrum of AC-tetraOH QxCav$_1$.

The calculated value of m/z for $C_{84}H_{80}O_{12}N_8$ is 1393.62 while the experimental value is 1393.59 and is relative to the protonate ion [M+ H^+]. The intensity of this peak is low, which indicates only the presence of traces of the product in the crude.

3.3 Obtaining the PIM-1 films

Finally, the PIM-1 films were made. The goal of making these films is to test, in the future, the different properties of these materials, and how these properties are affected when the films are made with crosslinked PIM-1 instead of from pure PIM-1. In this project, a crosslinked PIM-1 film was made using an OctaOH QxCav$_1$ (**Figure 19**), previously synthetized in our group in three synthetic steps.

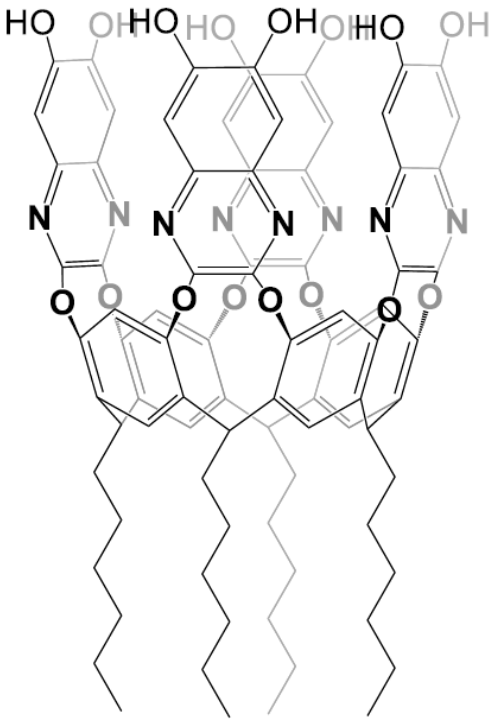


Figure 19: Structure of the OctaOH QxCav$_1$ used as crosslinker agent for crosslinked PIM-1.

The goal of the thesis was also to make a film using AC-tetraOH QxCav$_1$ but due to the difficulties in the synthesis, this part was not performed.

PIM-1 film preparation

For the preparation of the PIM-1 film, we followed a procedure found in literature[3].

The steps for the preparation of the film are the following:

- A solution of PIM-1 in chloroform was made (3% w/w). To increase the solubility, 1.14 g of PIM-1 was dissolved in 25 mL of chloroform at 60°C for 2 hours.
- The solution was casted in a Petri Dish (9 cm Ø) and put in a desiccator (**Figure 20A**).
- The evaporation of the solvent was allowed thanks to a flow of nitrogen in the desiccator for 24 hours.

The result is a yellow transparent film like the one shown in the **Figure 20B**.

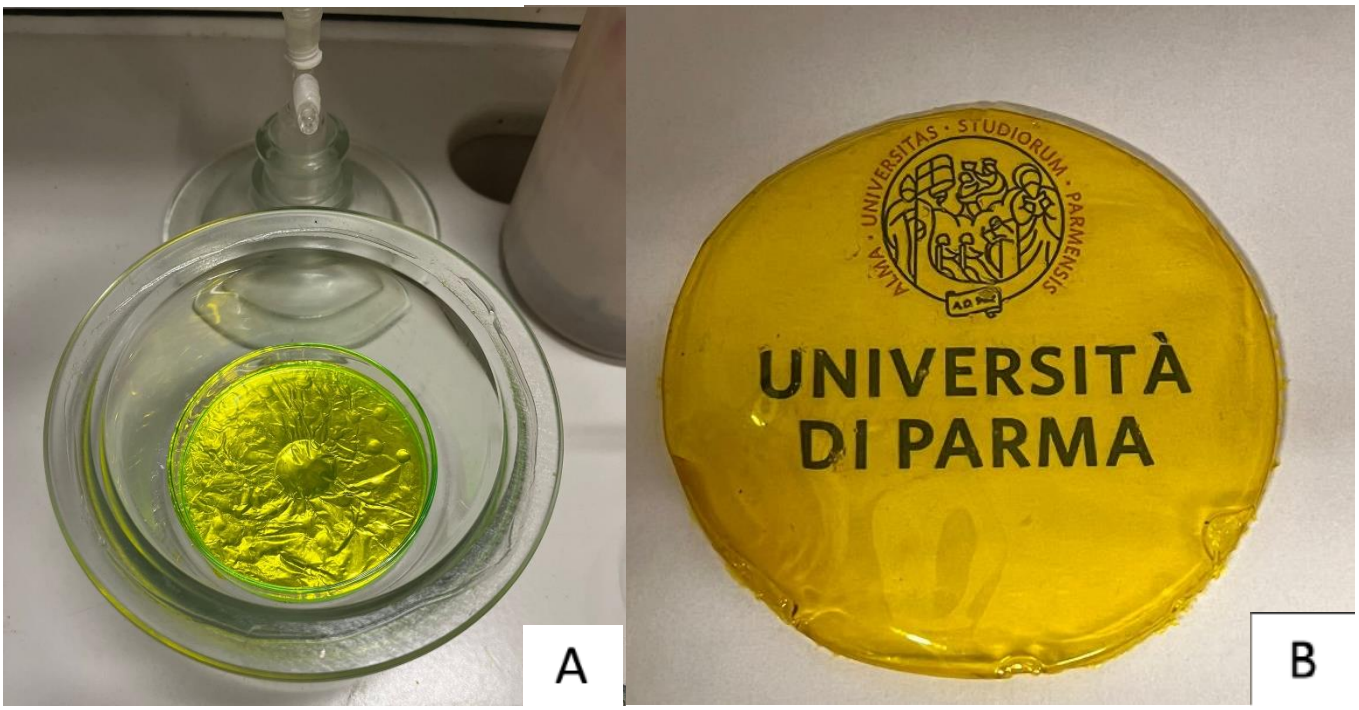


Figure 20: A) Desiccator set-up used to low evaporation of the solvent B) Photo of the PIM-1 film obtained.

Crosslinked-PIM1 Film (15% wt of QxCav-PIM-1):

The crosslinked PIM-1 polymer was already synthetized using the OctaOH $QxCav_1$ (5% mol) and was used for the preparation of the crosslinked PIM-1 (**Figure 21**) film.

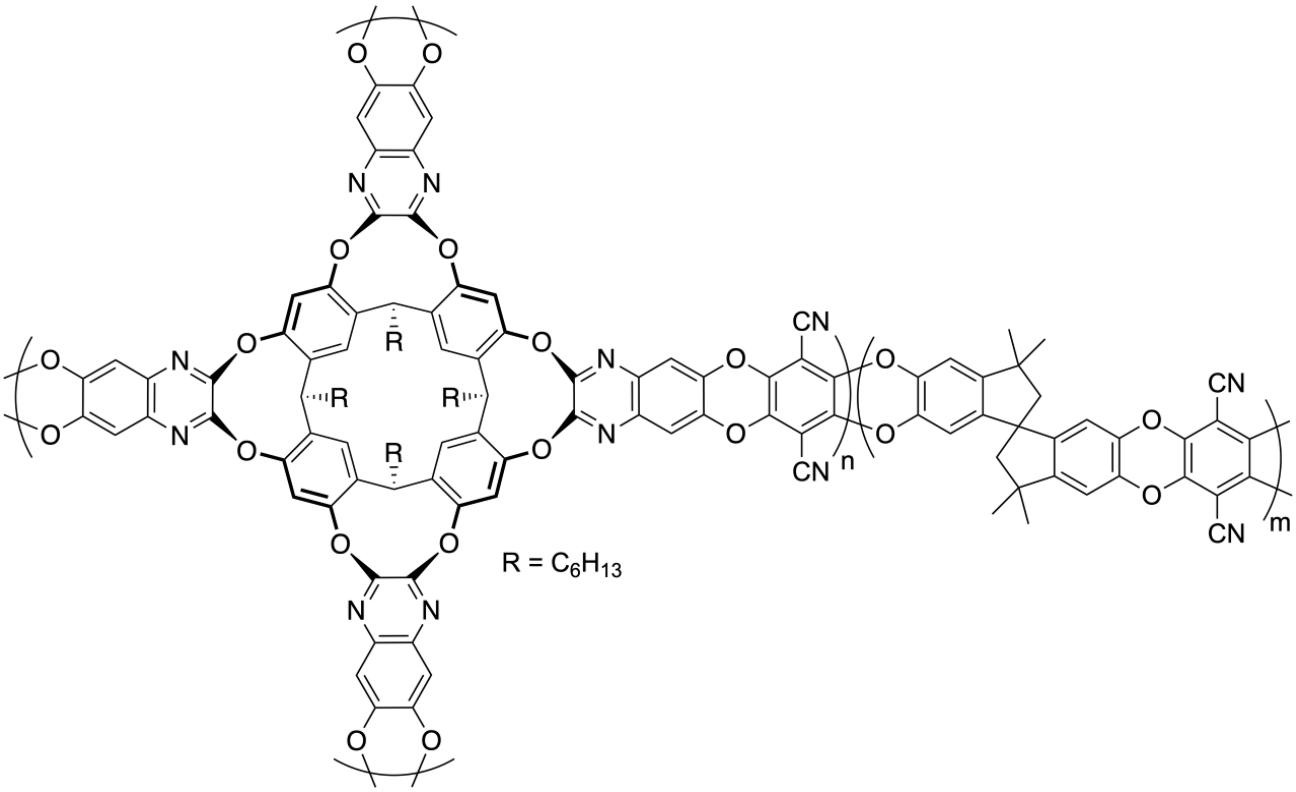


Figure 21: Structure of the crosslinked PIM-1 previously synthetized.

Since the polymer is not fully soluble in any solvent due to the crosslinking, the preparation of the film via simply solution casting of the polymer was not possible. Taking inspiration from a recent work of McKeown's groups[3], the steps for the preparation of the film are the following:

- A solution of PIM-1 in chloroform was made, 969mg of PIM-1 were dissolved in 15mL of chloroform while magnetically stirring at room temperature for 16 hours.
- 171mg of QxCav-PIM-1 were added to 15mL of chloroform, resulting in a yellow suspension that was stirred overnight.
- Both solutions were mixed in round-bottom balloon flask and stirred for 3 hours, followed by 30 minutes of probe sonication (**Figure 22A**)
- The sonicated solution (**Figure 22B**) was casted in a Petri Dish (9 cm Ø) and put in a desiccator.
- The slow evaporation of the solvent was possible thanks to a flow of nitrogen in the desiccator. It requires 24 hours.

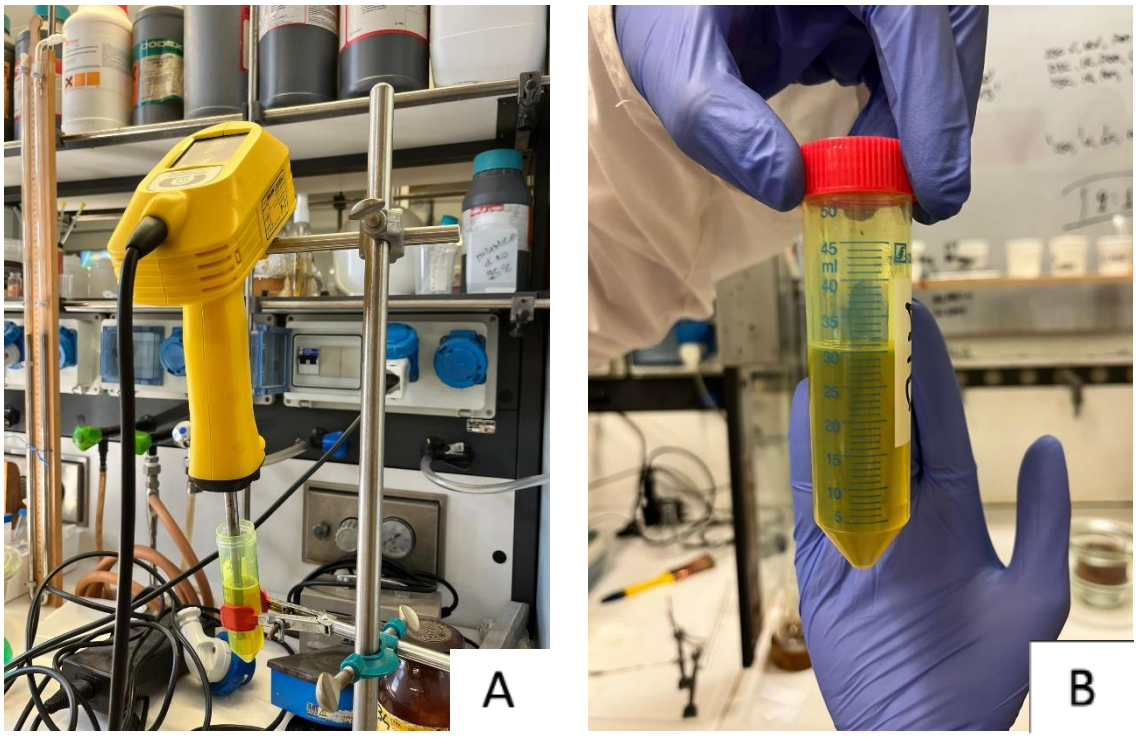


Figure 22: a) Probe sonicator used b) suspension resulting of 30 minutes of sonication.

The resulting film was reported in **Figure 23**.

Figure 23: Cross-linked PIM-1 film obtained.

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CONCLUSION

- PIM-1 was successfully synthetized using the low temperature method reported in literature[1]. The polymer was then characterized by ^{1}H-NMR spectroscopy and IR spectroscopy.

- PIM-1 film was obtained by slowly evaporating a solution of it in $CHCl_3$.

- The crosslinked PIM-1 film was satisfactorily obtained through blending method[3] by slow evaporation of the solvent using a mixture of 15% crosslinked PIM-1 (in weight) and 85% of regular PIM-1. This two films obtained will be compared in the future to know if the crosslinked one have some improvement over the regular one in terms of aging, plasticization and other mechanical properties.

- The first 3 steps for the synthesis of the new AC-TetraOH quinoxaline cavitand were successful and all the product was characterized through ^{1}H-NMR spectroscopy. However, during the last step (deprotection of methoxy group), after several purification the product was obtained in traces as MALDI-TOF shown. Different strategies will be used in future.

Experimental part

INSTRUMENTS, REAGENTS AND SOLVENTS USED

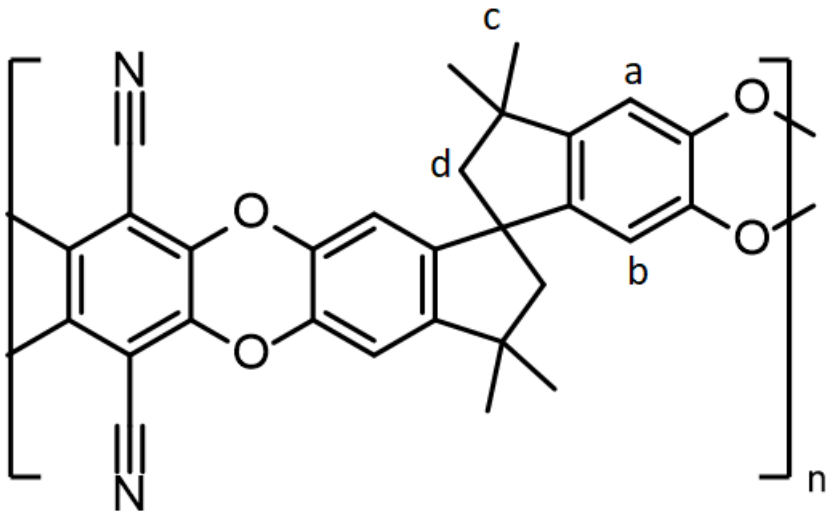
All reagents and solvents were purchased from certified commercial sources and were used without further purification, (otherwise it was specified). Solvents defined as anhydrous were treated following procedures known in literature or dried with previously activated 3 Å and 4 Å molecular sieves. The glassware for the reactions in anhydrous environment was anhydrified through vacuum / argon cycles. The yields were obtained by weighing the pure isolated product.

The progress of the reactions was verified by TLC thin layer chromatography MERK Analytical Chromatography F254®. Flash liquid chromatographs are performed using MERK 60 silica (0.04-0.063 mm / 230-400 mesh) following the method and technique proposed by Still.

$CDCL_3$, DMSO-d_6, acetone-d_6 and D_2O were used to obtain the 1H NMR spectra, recorded through the Bruker 400 AVANCE (400 MHz) or JEOL ECZ600R (600 MHz) spectrometers. The chemical shifts are expressed in ppm using tetramethylsilane or the residual peak of the solvent as internal reference. The terms s, d, t and m denote peaks of the singlet, doublet, triplet and multiplet spectrum, respectively

PIM-1 synthesis

In a two-necked bottom flask under dry conditions (3 vacuum/Ar cycles were done) were added 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindene (0.8g, 2.35mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (0.47g, 2.35mmol) in 100mL of DMF dry. At the end, 1.46g of K_2CO_3 were loaded to the reaction mixture. The reaction was set at 60ºC for 3 days while constant stirring. Finally, the reaction mixture was precipitated in water and the product was recovered by Büchner filtration. The resulting yellow polymer was purified dissolving 2 g of the powder in DCM and then precipitated from MeOH. The precipitate was then recovered by filtration on Büchner. Then, the solid obtained is loaded into a flask with a refrigerator containing distilled water and heated at 100ºC while constantly stirring for 3 hours. Finally, Büchner filtration allows to obtain 1 gram of yellow powdered product with an 80% yield.

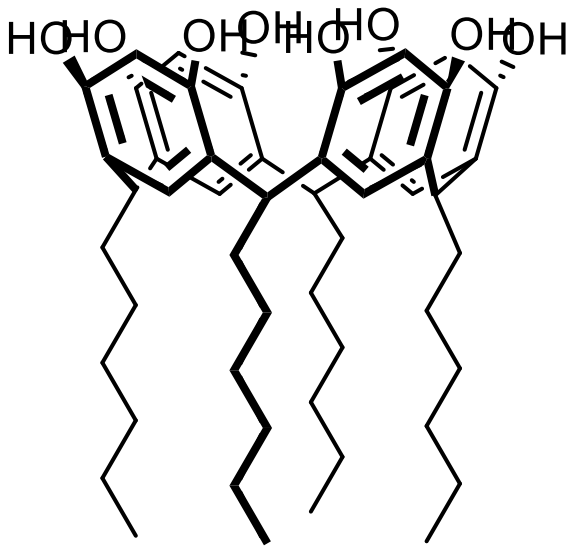


^{1}H NMR (400 MHz, Chloroform-*d*): δ (ppm) 6.83 (s, 2H, Ar**H_b**), 6.44 (s, 2H, Ar**H_a**), 2.35 – 2.18(m, 4H, **H_d**), 1.39 - 1.33 (m, 12H, **H_c**).

IR: ṽ (cm $^{-1}$) = 2956 (C-H sp^2, m), 2240 (C≡N, w), 1265 (C-O, s).

Synthesis of Res [C_6H_{13}, H]

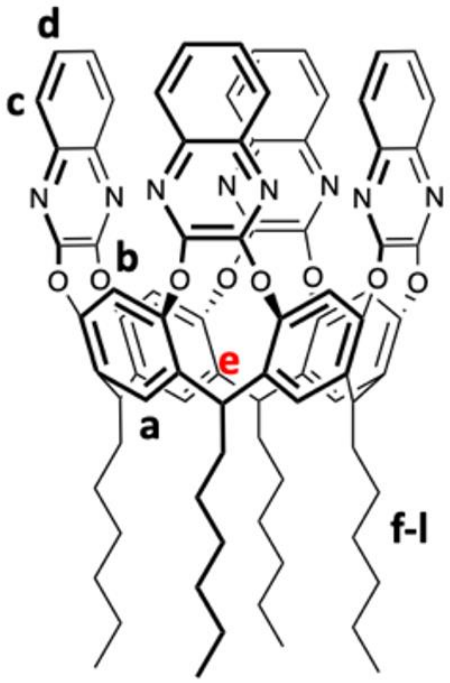
In a one-necked round bottom flask, 15 grams (0.14mol) of resorcinol were dissolved in 85mL of methanol, and then 23mL (0.16mol) of heptanaldehyde 98% were added to the solution, as well as 20mL of HCl 37%. The reaction was left overnight at 50°C over constant stirring. After this, the reaction mixture appeared reddish and was brought back to room temperature; it was also purified by acetonitrile recrystallization and dried in a vacuum oven to evaporate any trace of the solvent. Finally the crude was precipitated in methanol; obtaining a suspension where the solid part was yellowish. The solid was recovered by filtering on Büchner and washed with water several times. The product is thus obtained as a yellow powder-like solid.



^{1}H NMR (400 MHz, Acetone-d_6): δ(ppm) 8.45 (d, *J* = 1.9 Hz, 1H), 7.57 (s, 1H), 6.25 (s, 1H), 4.36 – 4.28 (m, 1H), 3.36 – 3.29 (m, 4H), 3.16 – 3.07 (m, 1H), 2.88 – 2.78 (m, 6H), 2.31 (q, *J* = 7.7 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.31 (tdd, *J* = 10.9, 7.5, 4.9 Hz, 7H), 0.90 (t, *J* = 6.9 Hz, 3H).

Synthesis of the $QxCav_1$

In a two-necked flask previously dried (3 cycles Ar/vacuum), 2.02g (2.38mmol) of **Res [C_6H_{13},H]** were dissolved in 40mL of DMF dry and then 2.08g (10.46mmol) of K_2CO_3 were added. The mixture was stirred for 10 minutes, then the mixture turned dark red. At the end, 1.97g (14.26mmol) of 2,3-dichloro-quinxaline were added; the solution appeared dark pink. The reaction was allowed to react at 80°C overnight for 16 hours. The brown suspension obtained was precipitated in 400mL of water and then filtered on Büchner. The crude was purified by column chromatography (eluent hexane/EtOAc 8:2).

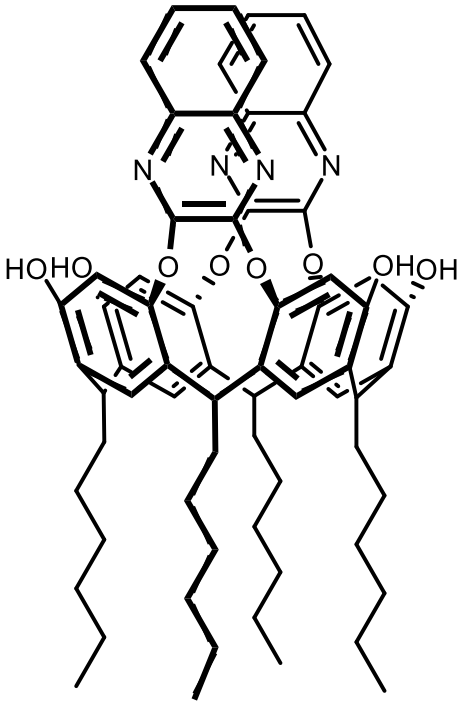


^{1}H NMR ($CDCL_3$, 400MHz): δ(ppm) 8,18 (s, 4H, Ar-O**H$_o$**), 7,82 (q, 8H, Ar**H$_c$**), 7,49 (d, 8H, Ar**H$_d$**), 7,26 (s,4H, CH_2=C**H$_a$**), 5,59 (t, 4H, **H$_e$**), 2,3 (dd, 4H,**H$_f$**), 2,07 (t, 4H, ArC**H$_g$**, J=7,9 Hz), 2,02 (q, 8H, ArCHC**H$_h$**, J=6,8 Hz), 1,39 (m, 56H, C**H$_{2\ h\text{-}n}$**)

Synthesis of AC QxCav$_1$:

In a one-necked round bottom flask 500mg (0.37 mmol) of the quinoxaline cavitand$_1$ were dissolved in 80mL of DMF, then 1.14g (7.52 mmol) of CsF were added. The mixture was heated at 80°C. Separately, a solution of 133mg (1.2 mmol) of Catechol in 20mL of DMF was prepared. This solution was added to the hot reaction mixture using a dripping funnel and let react for 40'. The reaction mixture was then precipitated in cold brine, and the grey precipitate was filtered by Büchner filtration. The crude product was then purified via column chromatography using DCM/EtOAc 95/5 -> 85/15 as eluent.

The product was recovered as a white solid with a yield of 41%

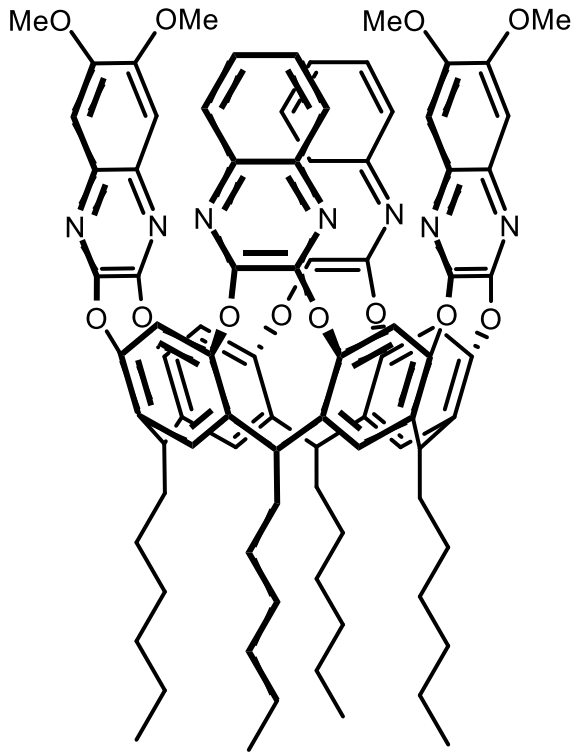


^{1}H NMR (400 MHz, Acetone-d_6) δ 8.99 (s, 1H), 7.83 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.74 (s, 2H), 7.66 (dt, *J* = 6.4, 3.2 Hz, 2H), 7.19 (s, 2H), 5.52 (t, *J* = 8.3 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 3H), 2.83 – 2.78 (m, 14H), 2.39 (q, *J* = 7.5 Hz, 4H), 1.98 (s, 4H), 1.43 (s, 4H), 1.38 – 1.28 (m, 10H), 1.21 (t, *J* = 7.1 Hz, 5H), 0.92 (td, *J* = 6.8, 1.2 Hz, 6H).

Synthesis of AC-OMe QxCav$_1$:

In a dry MW tube, 150mg (0.139 mmol) of AC-QxCav$_1$ were dissolved in 6mL of DMF dry under constant stirring. The addition of 192mg (1.39 mmol) of K_2CO_3 turned the color of the solution to orange. After 10 minutes, add 83.1mg (0.321mmol) of 2,3-dichloro-6,7-dimethoxy quinoxaline to the tube, the solution became darker. The reaction proceeded in MW at 120^{o}C for 1 hour and 35 minutes.

After that, the solvent was removed under vacuum and the crude solid purified by column chromatography using DCM/EtOAc 95/5 as eluent. Finally, 100mg of product were isolated as a white powder.



^{1}H NMR (600 MHz, Chloroform-*d*), δ(ppm): 8.11 (s, 2H), 7.78 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.38 (dt, *J* = 6.2, 3.5 Hz, 2H), 7.25 (s, 8H), 7.21 (s, 2H), 7.11 (s, 2H), 5.59 (d, *J* = 8.5 Hz, 1H), 5.56 (d, *J* = 8.4 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 3H), 4.02 (s, 6H), 2.25 (q, *J* = 7.9 Hz, 4H), 2.03 (d, *J* = 0.8 Hz, 4H), 1.54 (s, 12H), 1.46 (d, *J* = 7.2 Hz, 4H), 1.36 – 1.29 (m, 8H), 1.25 (td, *J* = 7.1, 0.7 Hz, 5H), 0.91 (td, *J* = 7.0, 1.4 Hz, 6H).

Deprotection of AC-OMe QxCav$_1$:

In a schlenk (with a volume much bigger than the volume of solvent used, in this case, a 100mL one was used), add the previously weighed reagent and the solvent under dry conditions (3 cycles vacuum/Ar). Then add the BBr3 carefully. Keep the reaction stirring while maintaining the dry conditions. After 4 hours the reaction was checked with TLC and it was then decided to leave it reacting overnight. The next day the reaction was quenched in water and MeOH acquiring a pale yellow colour. After this, the chloroform and methanol were removed using a vacuum trap and finally some acidic water was added, and the product was filtered in a Buchner and characterised by 1H-NMR.