coatings

1st Coatings and Interfaces Web Conference 2019

“Application of Calixresorcinarenes as Chemical Sensors”

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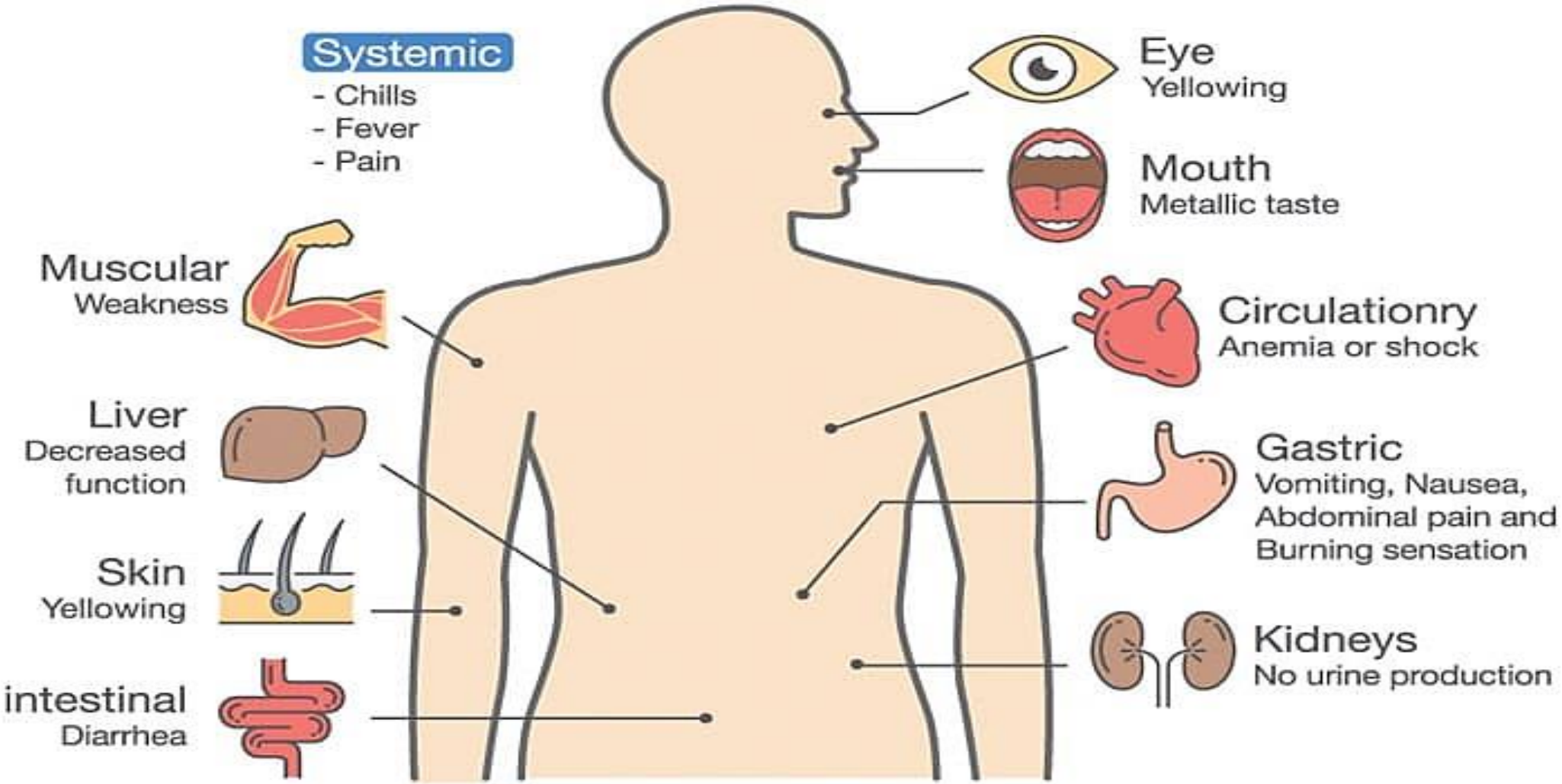
Introduction

Introduction



Conventional methods for heavy metals detection

Inductively coupled plasma/atomic emission spectrometry (ICP-AES)

Inductively coupled plasma/mass spectrometry (ICP-MS)

Atomic absorption spectroscopy (AAS)

Conventional methods for heavy metals detection

Expensive,

Sample preparation,

Professional skills….etc.

SOLUTION

Lab-on-chip technology

Materials & methods

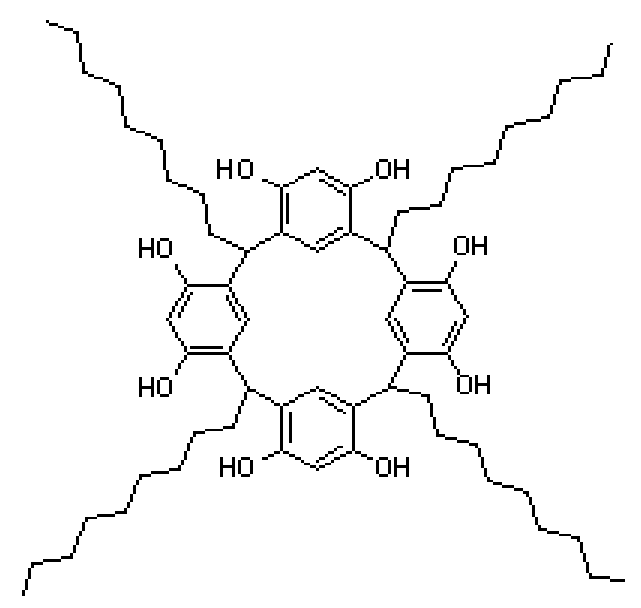
Synthesis of macrocycles

Their synthesis is based on the condensation between para-substituted phenols/resorcinols and aldehydes

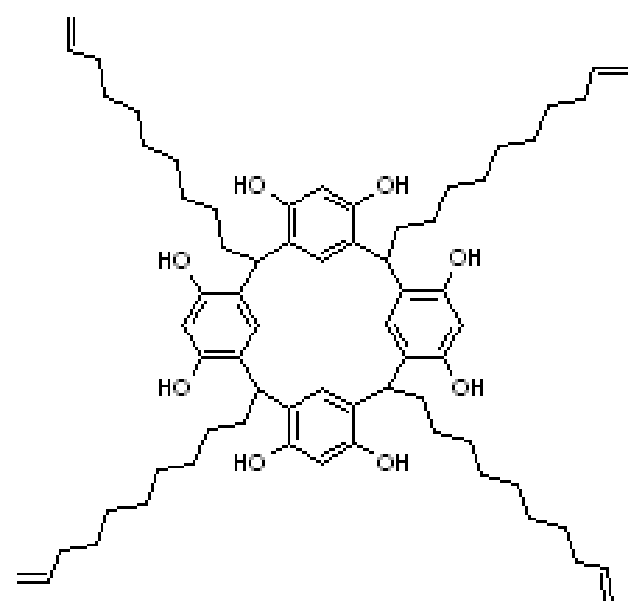
- **CAL 11 U**: C-dec-9-en-1-ylcalix[4]resorcinarene,
- **CAL 9U**: C-trans-2, cis-6-octa-1,5-dien-1-ylcalix[4]resorcinarene,
- **CAL 10**: C-nonylcalix[4]resorcinarene.

Materials & methods

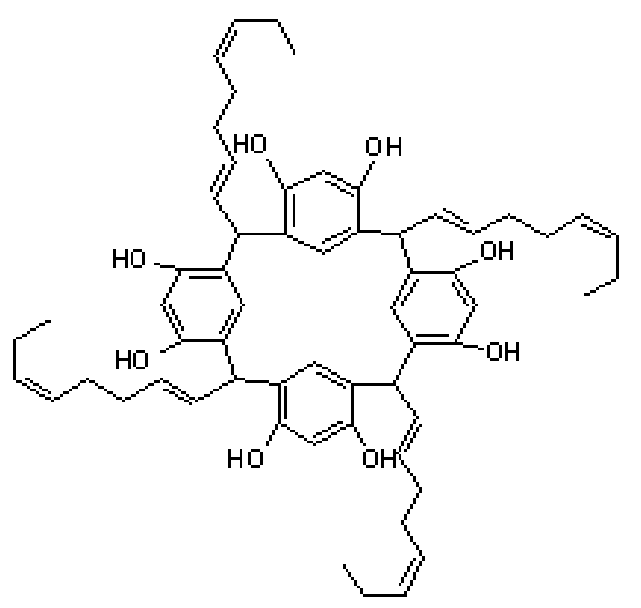
Synthesis of macrocycles



(a)



(b)



(c)

Figure 1. Molecular structures of the synthetized calix[4]resorcinarenes : **(a)** C-nonylcalix[4]resorcinarene; **(b)** C-dec-9-en-1-ylcalix[4]resorcinarene; and **(c)** C-trans-2, cis-6-octa-1,5-dien-1-ylcalix[4]resorcinarene .

Materials & methods

Characterization of macrocycles

Melting points

determination

FTIR :

To define the functional groups

TG-DSC-MS:

To study the thermal behavior

XRD:

To evaluate the degree of crystallinity

1H NMR & 13C NMR:

To confirm the proposed structure

Results & discussion

Characterization of macrocycles

Melting points determination

Table 1. Experimental melting points of the synthesized molecules.

Molecule code	Molecule name	Melting point (^{0}C)	Weight after grinding (g)
CAL 11U	C-dec-9-en-1-ylcalix[4]resorcinarene	277.0	2.9434
CAL 9U	C-trans-2, cis-6-octa-1,5-dien-1-ylcalix[4]resorcinarene	Till 314.0 (No thermal event)	1.0644
CAL 10	C-nonylcalix[4]resorcinarene	284.6	0.0300

Results & discussion

Characterization of macrocycles

FTIR measurements (*To determine the functional groups*)

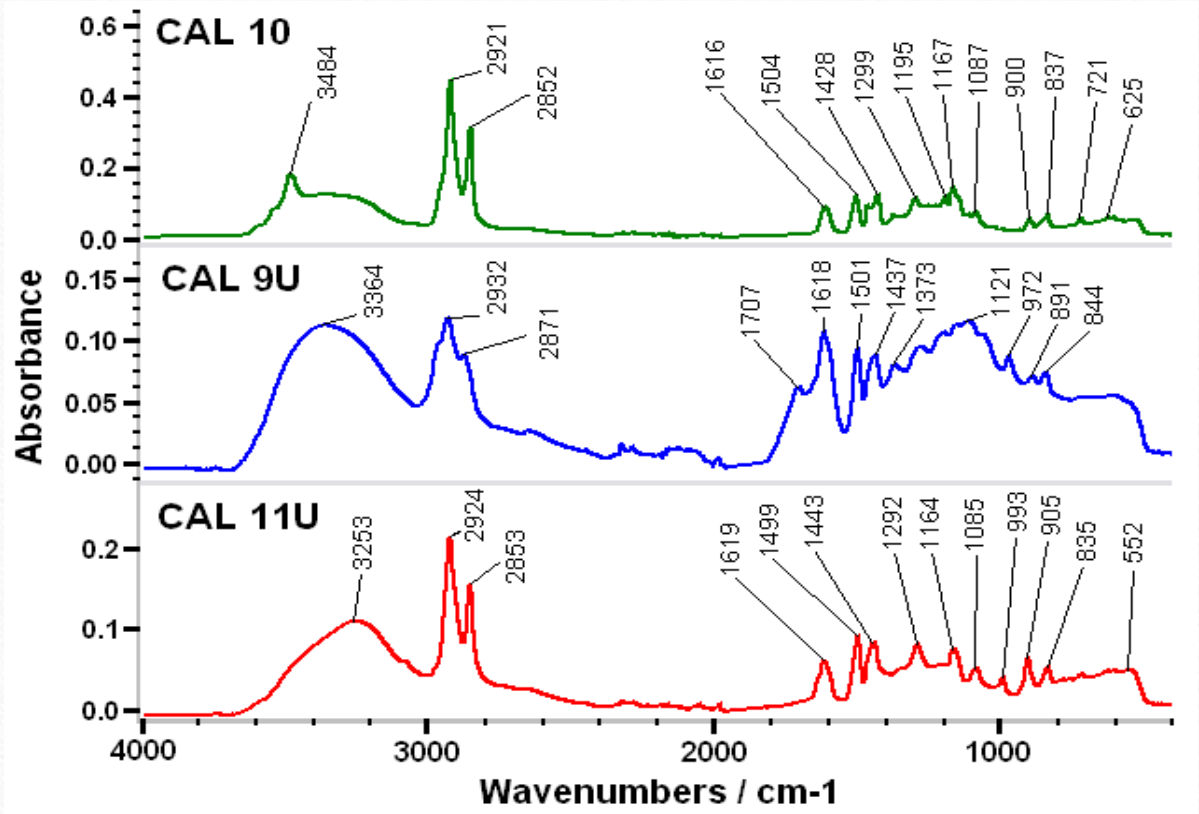


Figure 2. FTIR spectra of the macrocycles

Results & discussion

Characterization of macrocycles

FTIR measurements

Table 2. IR parameters of CAL 11U.

Molecule parts	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	3253	Associated O-H	Stretching	Strong and large
	1164	C-O	Stretching	Medium
	1292	O-H	In plan deformation	Medium
Vinyl	3077 3034 1822 1619	=C-H =C-H C-H C=C	Stretching Stretching Deformation harmonics Stretching	Medium Medium Medium Medium
Aromatic	3074 1499 1443 1980 835	=C-H C=C C=C C-H C-H	Stretching Stretching Stretching Deformation harmonics Out plan deformation	Medium Medium Medium Small Medium to small
Alkane	2924 2853 721	CH_2	Asymmetric stretching Symmetric stretching Rocking	Strong Medium Medium to small

Results & discussion

Characterization of macrocycles

FTIR measurements

Table 3. IR parameters of CAL 9U

Molecule parts	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	3364	Associated O-H	Stretching	Strong and large
	1201	C-O	Stretching	Strong
	1373	O-H	In plan deformation	Strong
Aromatic	1598	C=C	Stretching	Small
	1560	C=C	Stretching	Small
	1501	C=C	Stretching	Medium
	1437	C=C	Stretching	Medium
	1707	C-H	Deformation harmonics	Small
	891	=C-H	Out plan deformation	Medium
Alkene	1652 } Trans	C=C	Stretching	Medium
	727 } Trans	=C-H	Out plan deformation	Medium
	1683 } Cis	C=C	Stretching	Medium
	1288 } Cis	=C-H	In plan deformation	Medium
	972	=C-H	Out plan deformation	Strong
	1618	C=C	Stretching	Strong
Alkane	2932	CH_2	Asymmetric stretching	Strong
	2871	CH_3	Symmetric stretching	Strong
	1437	CH_3	In plan deformation	Medium
	729	CH_2	Rocking	Medium

Results & discussion

Characterization of macrocycles

FTIR measurements

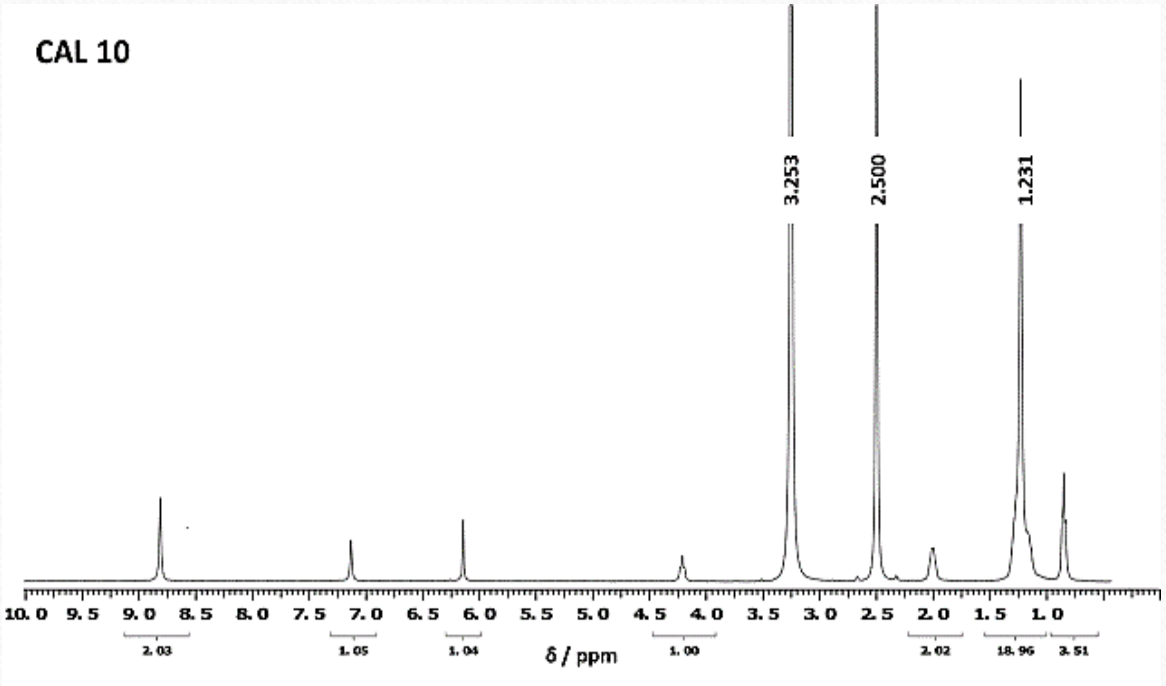
Table 4. IR parameters of CAL 10

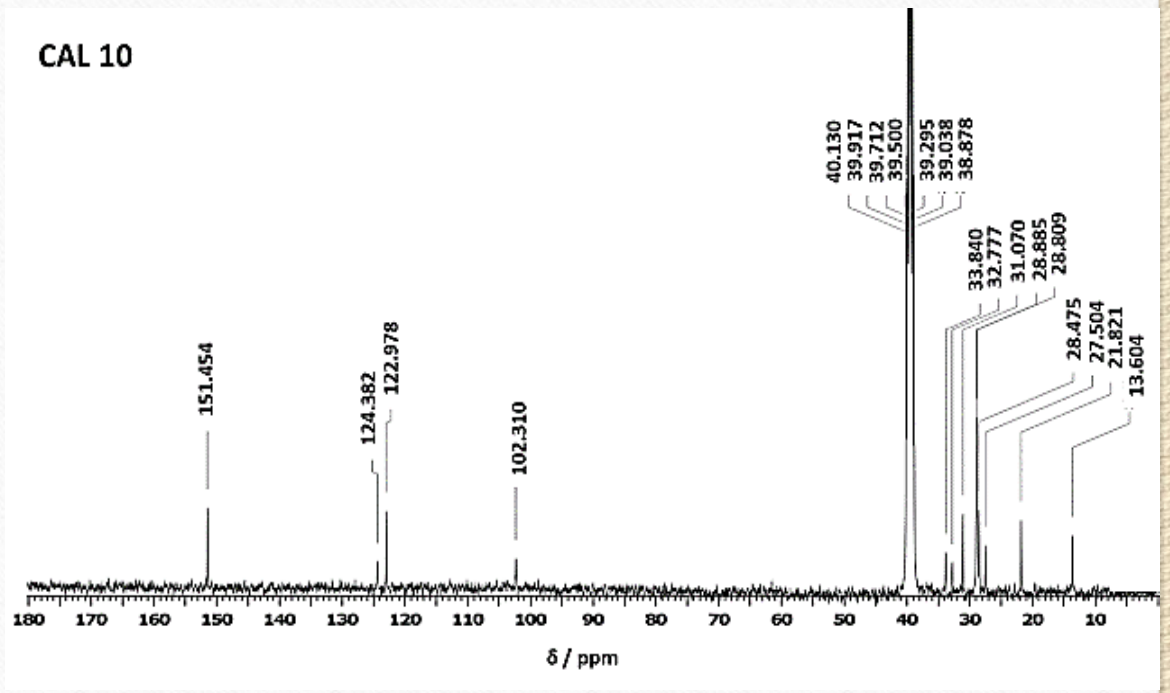
Molecule parts	Wave number (cm^{-1})	Bond	Nature of vibration	Intensity
Resorcinol	3484	Associated O-H	Stretching	Strong & large
	1195	C-O	Stretching	Medium to strong
	1377	O-H	In plan deformation	Medium
Aromatic	3038	=C-H	Stretching	Very small
	1616	C=C	Stretching	Medium
	1504	C=C	Stretching	Medium
	1464	C=C	Stretching	Medium
	1979	C-H	Deformation harmonics	Small
	900	=C-H	Out plan deformation	Small
Alkane	2852	CH_3	Symmetric stretching	Strong
	1428	CH_3	Asymmetric plan deformation	Medium
	2921	CH_2	Asymmetric stretching	Strong
	1465	CH_2	Scissoring	Medium
	721	CH_2	Rocking	Medium
	1342	C-H	In plan deformation	Very small
	1167	Linear chain C-C	Stretching	Small

Results & discussion

Characterization of macrocycles

NMR Analysis (*To confirm the chemical structure*)



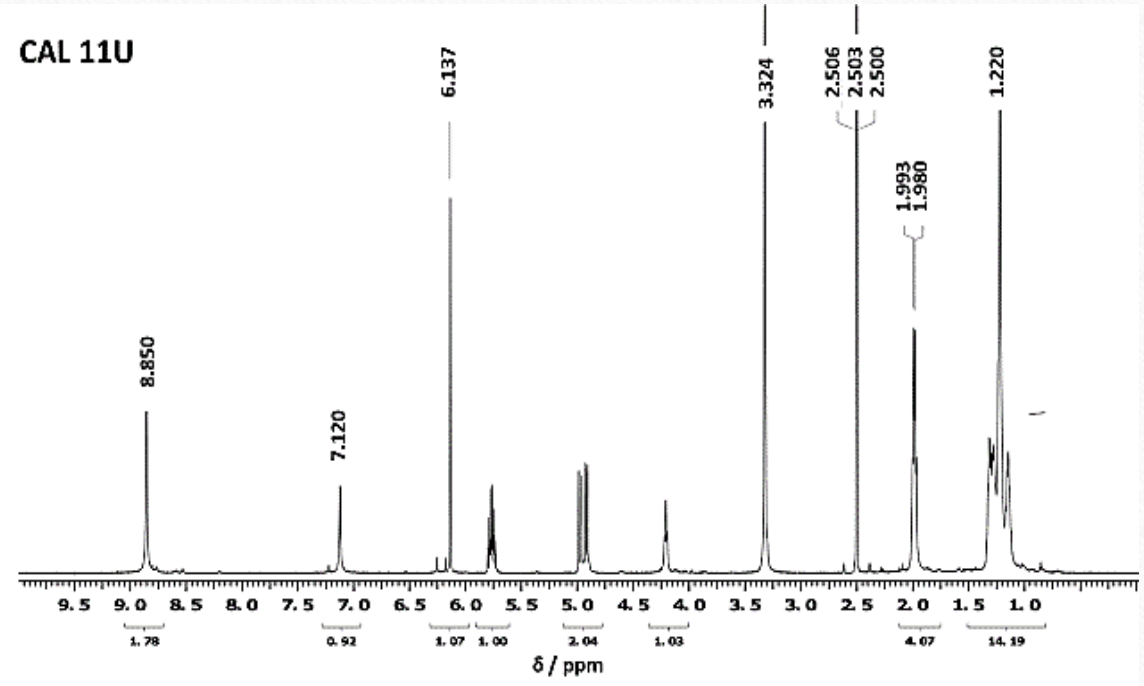


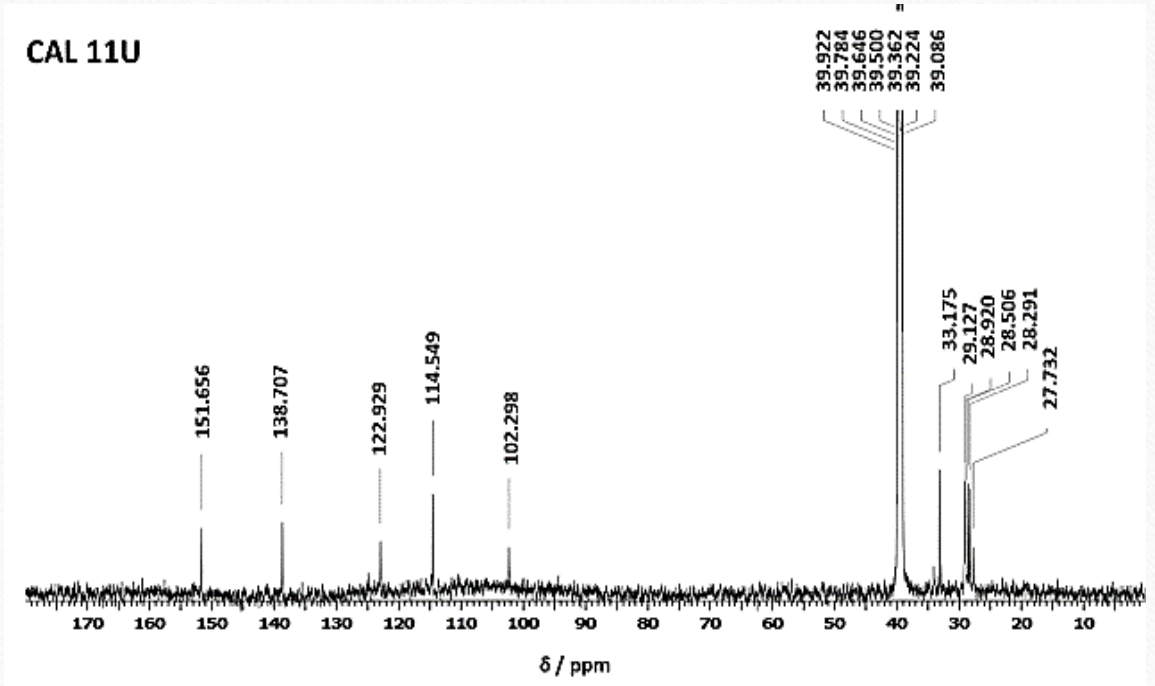
Figures 3,4. ^{1}H NMR and ^{13}C NMR spectra of CAL 10

Results & discussion

Characterization of macrocycles

NMR Analysis





Figures 5,6. ^{1}H NMR and ^{13}C NMR spectra of CAL 11U

Results & discussion

Characterization of macrocycles

NMR Analysis

CAL 10

^{1}H NMR (DMSO-d6, 400 MHz, 40 °C) δ (ppm): 8.75 (8H, s); 7.12 (4H, s); 6.13 (4H, s); 4.23 (4H, t, J = 8.0Hz); 2.02 (8H, m); 1.47 – 1.00 (56H, m); 0.82 (12H, t, J = 6.3Hz).

^{13}C NMR (DMSO-d6, 100 MHz, 50 °C) δ (ppm): 151.5; 124.4; 123.0; 102.3; 33.8; 32.8; 31.1; 28.9; 28.8; 28.5; 27.5; 21.8; 13.6.

CAL 11U

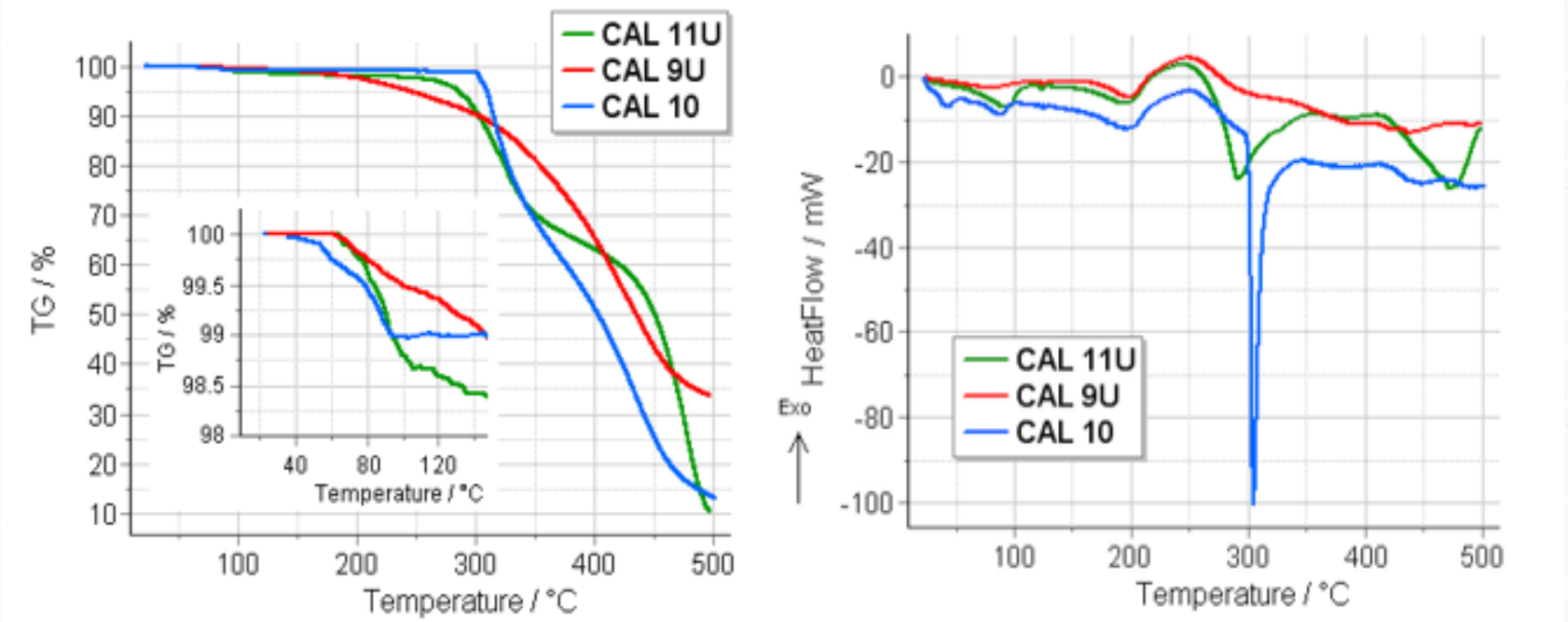
^{1}H NMR (DMSO-d6, 600 MHz, 25 °C) δ (ppm): 8.85 (8H, s); 7.12 (4H, s); 6.13 (4H, s); 5.75 (4H, m); 4.98 (4H, m); 4.92 (4H, m); 4.22 (4H, t, J = 8.3Hz); 2.07 – 1.97 (16H, m); 1.43 – 1.05 (48H, m).

^{13}C NMR (DMSO-d6, 150 MHz, 25°C) δ (ppm): 151.7; 138.7; 124.7; 122.9; 114.5; 102.3; 33.2; 33.0; 29.2; 29.1; 28.9; 28.5; 28.3; 27.7.

Results & discussion

Characterization of macrocycles

TG-DSC-MS Investigations (*To study the thermal behavior*)



(a) **(b)**

Figure 7. The results of thermogravimetric (7a), and differential scanning calorimetric (7b) measurements (the inset in figure 7a is a magnification of the TG curve from the beginning of the measurement up to 150 °C).

Results & discussion

Characterization of macrocycles

TG-DSC-MS Investigations

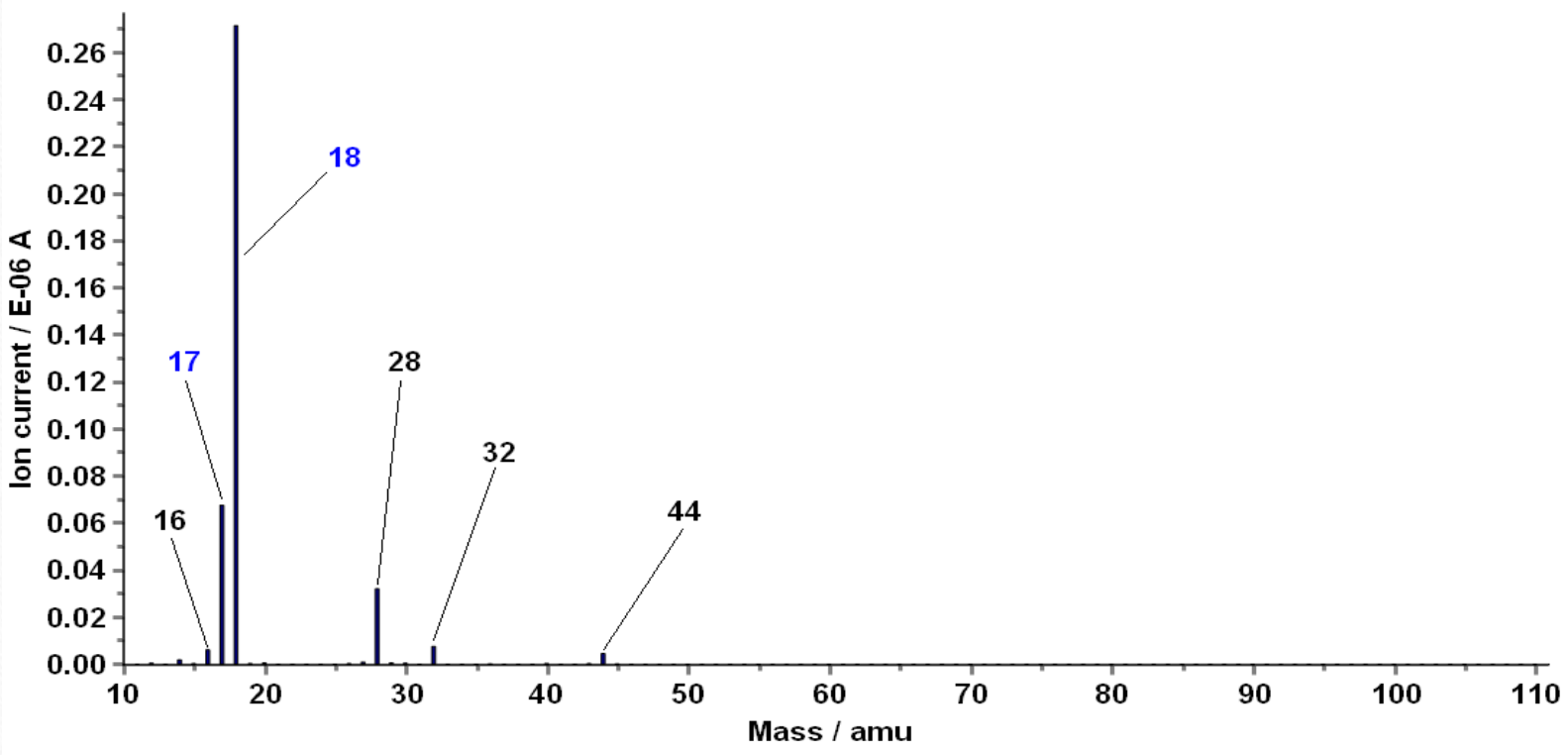


Figure 8. Mass spectra of the evolved volatiles form sample CAL 10, at 87 °C

Results & discussion

Characterization of macrocycles

TG-DSC-MS Investigations

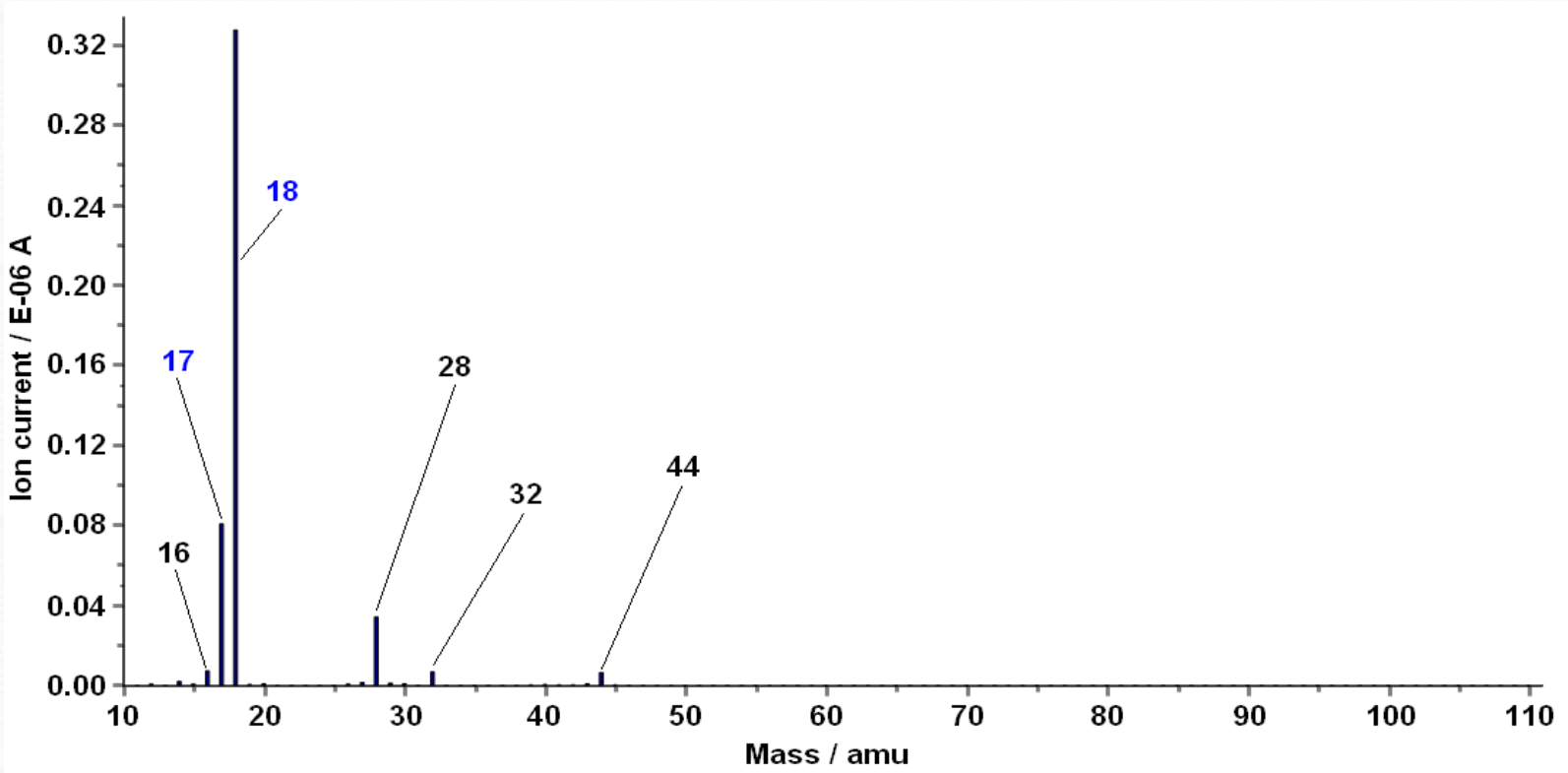


Figure 9. Mass spectra of the evolved volatiles form sample CAL 9U, at 83 °C

Results & discussion

Characterization of macrocycles

TG-DSC-MS Investigations

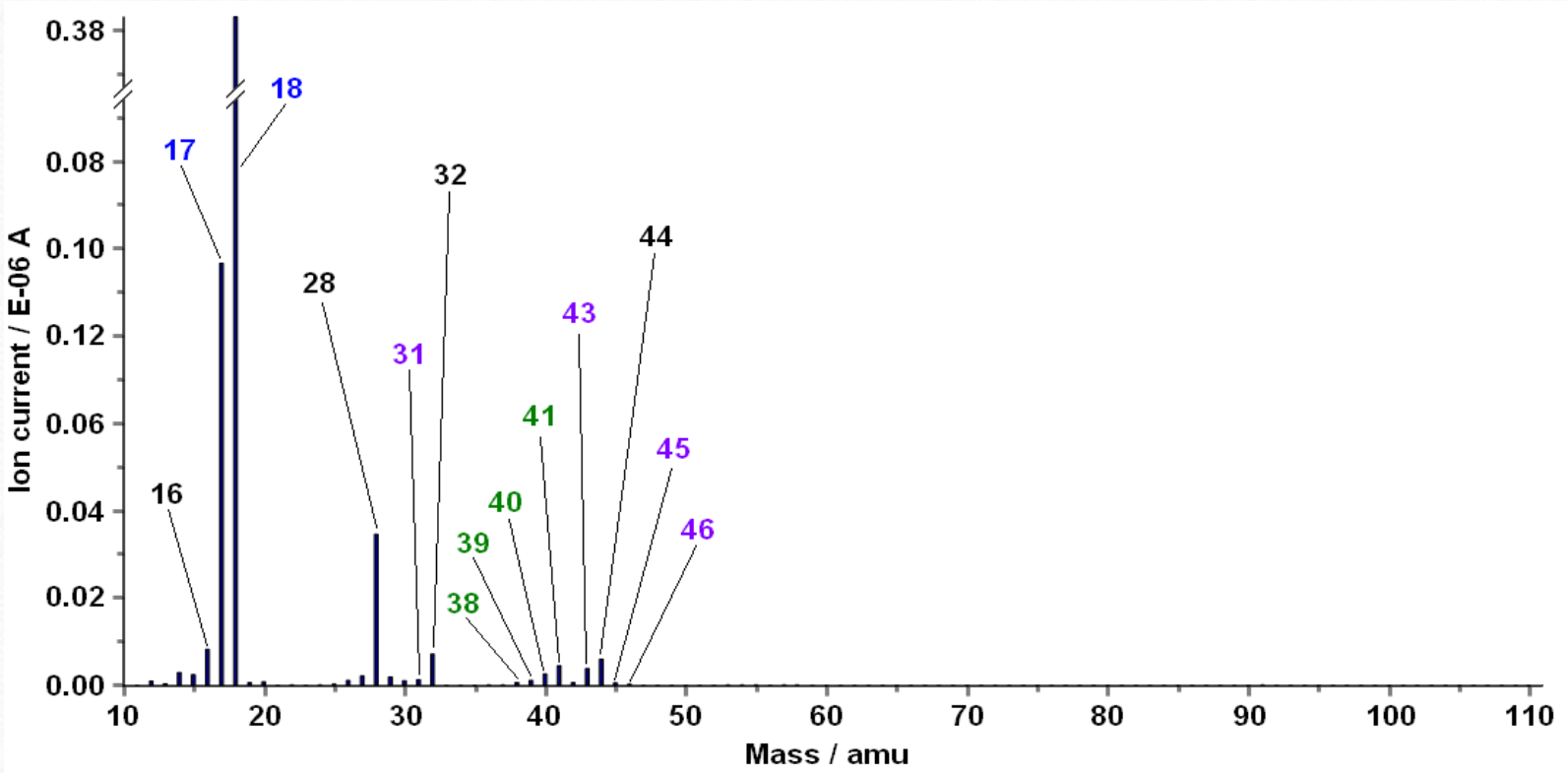


Figure 10. Mass spectra of the evolved volatiles form sample CAL 11U, at 92 °C

Results & discussion

Characterization of macrocycles

Powder XRD studies (To investigate the crystallinity degree)

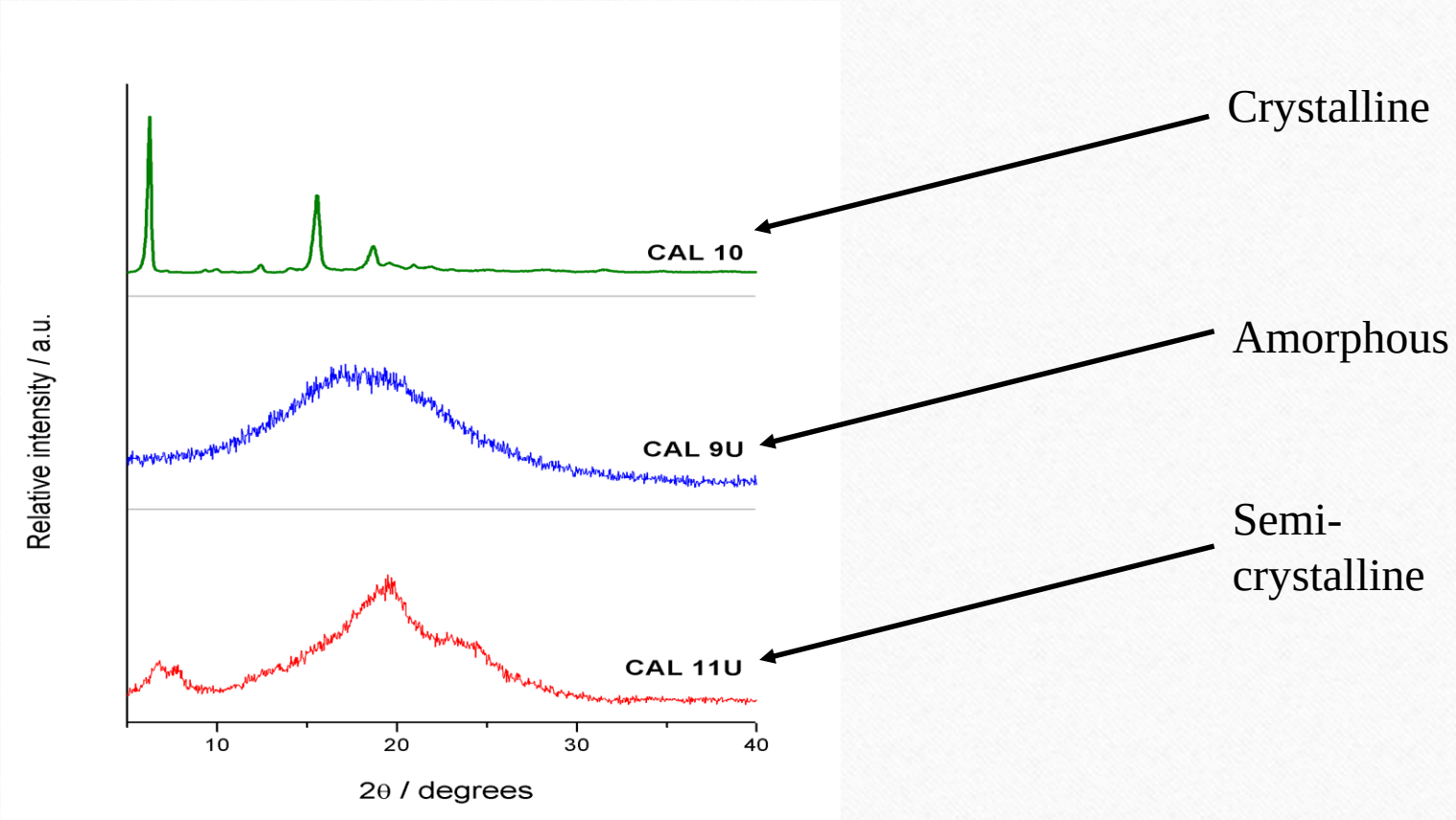


Figure 11. Powder X-ray diffractograms of the three calix[4]resorcinarenes

Results & discussion

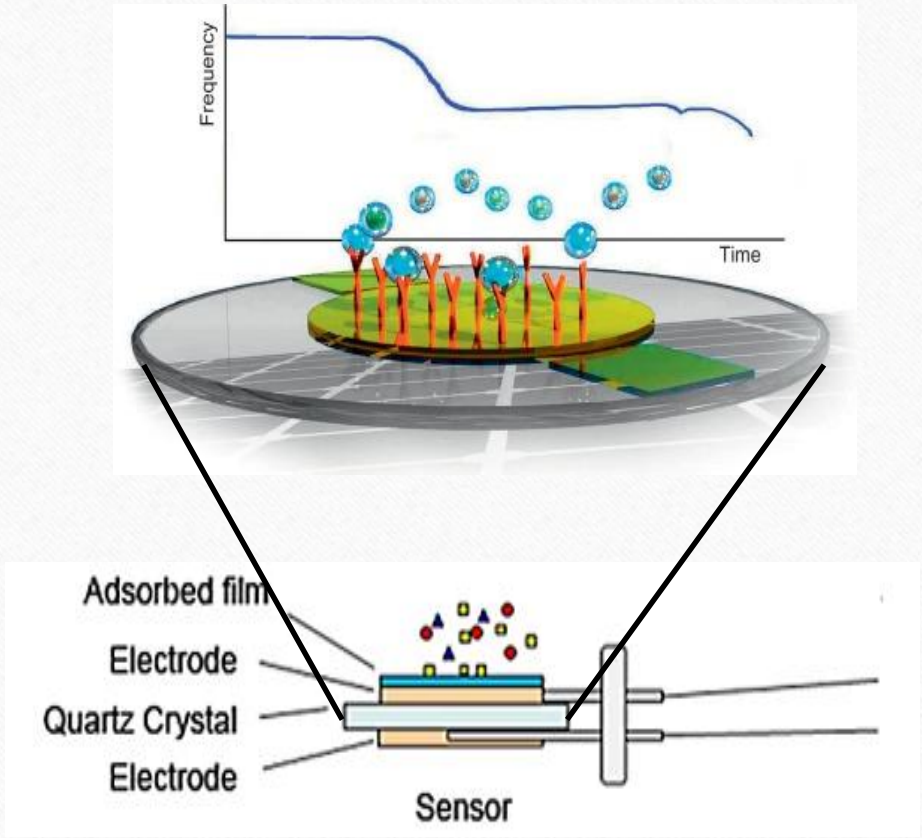
Characterization of macrocycles

Conclusion

The ***melting points*** of the synthesized molecules were between 277 and 314 ^{0}C, their ***FTIR*** spectra showed all the functional groups of the structures, furthermore the ***NMR*** studies confirmed the proposed structures, the ***TGA-DSC-MS*** analysis gave the same range of melting points found directly, also they demonstrated that the calixresorcinarenes are pure, by analyzing the results of the mass spectrometric evolved gas analysis ***(MS-EGA)***, the volatiles released from the samples were exclusively water, some traces of ethyl alcohol and acetonitrile were found also, they are due to the preparation process, besides the Powder ***XRD*** patterns showed that CAL 10 is totally crystalline, that CAL 11U is a mixture of amorphous and crystallized fractions, and that CAL 9U is practically amorphous.

Results & discussion

QCM-I studies



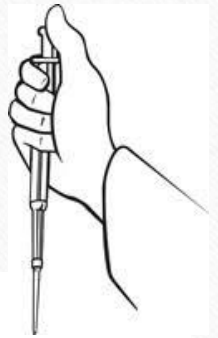
Frequency changes according to adsorption of chemicals on the QCM Surface

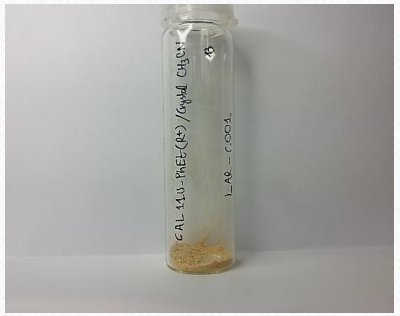
QCM-I 008 Unit

Results & discussion

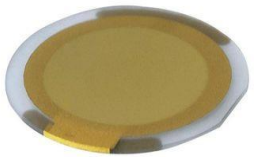
QCM-I studies

10 µL Coated





Calix. Solution 2 mg/ml



Clean Quartz Crystal

To detect

Heavy metal solution { 200 ppm of Lead nitrate $Pb(NO_3)_2$

Results & discussion

QCM-I studies

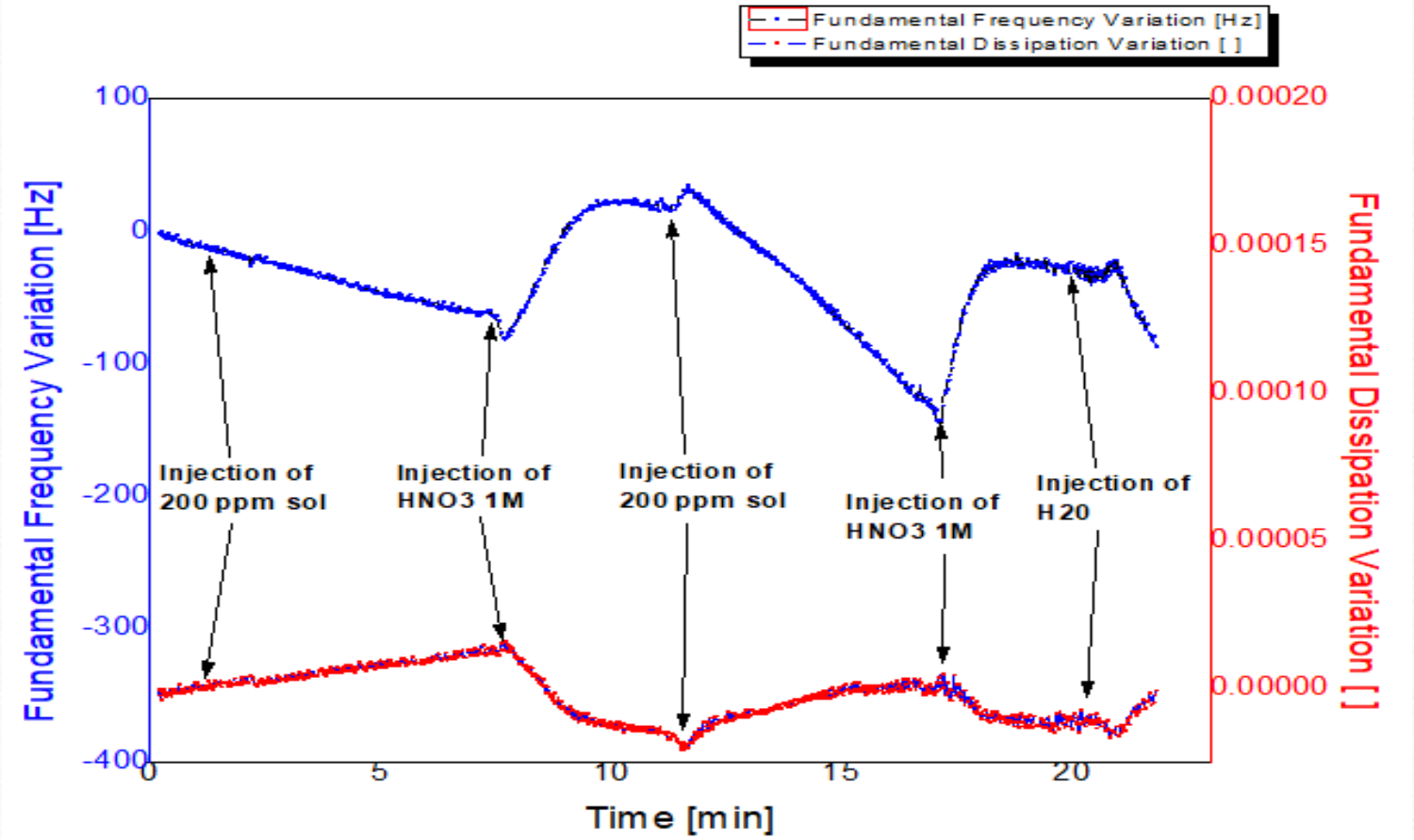


Figure 12. Variation of fundamental frequency, and fundamental dissipation energy due to the injection of heavy metals solution in time.

Conclusions

- ✓ A series of calixresorcinarene macrocycles were synthesized by a simple condensation reaction, they were characterized by different techniques (Melting points determination, NMR, FTIR, TG-DSC-MS, and XRD).

- ✓ The quartz crystal microbalance (QCM) is a nanogram sensitive technique that utilizes acoustic waves generated by oscillating a piezoelectric single crystal quartz plate to measure mass. The results of the application of calixresorcinarene macrocycles as sensing platforms showed the usefulness of this technique for the detection of heavy metal ions (Lead nitrate) at very low level (ppm).

References

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Thank you for your attention