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Calix[4]resorcinarene macrocycles

Synthesis, thermal behavior and crystalline characterization

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Abstract

Supramolecular chemistry is an interdisciplinary scientific field, including chemical, physical and biological properties of more complex chemical species than the molecules themselves. Calixarenes/calixresorcinarenes are macrocyclic compounds, consisting of 'n' phenolic/resorcinolic units linked together by methylene bridges; these macrocycles are often used for molecular recognition. Thus, different modifications can be made to both the lower and upper rim, allowing the construction of well-defined multivalent buildings. In this work, three calix[4]resorcinarene macrocycles were synthesized, namely C-dec-9-en-1-ylcalix[4]resorcinarene (CAL 11U), C-trans-2, cis-6-octa-1,5-dien-1-ylcalix[4]resorcinarene (CAL 9U) and C-nonylcalix[4]resorcinarene (CAL 10) by a simple condensation reaction. The compounds CAL 11U and CAL 10 have been already synthesized by researchers, while the CAL 9U has been synthesized for the first time. Their structures were confirmed using ATR-FTIR, ^{1}H NMR and ^{13}C NMR. Thermal analysis combined with mass spectrometric evolved analysis of the vapors was used to study the thermal behavior of the different synthesized molecules, and they were the subject of characterization by X-ray powder diffraction in order to analyze their degree of crystallinity.

Keywords Calixresorcinarenes · Thermal analysis · FTIR · XRD · Synthesis

Introduction

A calixarene/calixresorcinarene is a macrocyclic molecule composed of 'n' phenolic/resorcinolic units connected to each other by a methylene bridge located in the ortho position to the hydroxyl group as shown in Fig. 1. Their synthesis is based on the condensation between para-substituted phenols/resorcinols and aldehydes [1].

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Calix[4]arenes/calix[4]resorcinarenes are a target for researchers in supramolecular science examinations, because of their receptor properties or host–guest behavior, due to the distinct hydrophilic lower rim and the hydrophobic upper rim. The calixarene's/calixresorcinarene's upper rim forms the 'entry' to the cavity; this cavity has a hydrophobic character. Due to these properties, those macrocycles are amphiphilic.

Generally, calix[4]arene/calix[4]resorcinarene molecules can form polymers by intermolecular hydrogen bonds between hydroxyl groups. Figure 2 concerns the conformers of calix[4]resorcinarene, such as: 'chair,' 'boat' and 'cone' conformations. The capacity of these molecules to entrap different molecules/ions determines the applicability calix[4]arenes/calix[4]resorcinarenes. It is inferred that they contain some amount of water or solvent traces, which are retained from the preparation process. The number of reports on calixarenes/calixresorcinarenes is enormous [2–7]; they are mainly applied as extractants [8–31] and sensors [32–38].

Characterization of calixarenes/calixresorcinarenes layers to be applied as sensors is carried out by several methods such as thermal analysis [39–47].

Fig. 1 **a** Molecular structure of calix[4]resorcinarene, **b** molecular structure of calix[4]arene
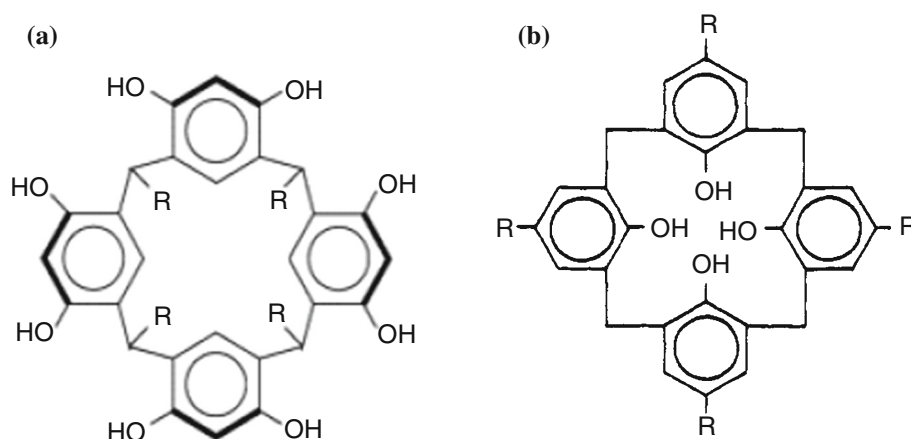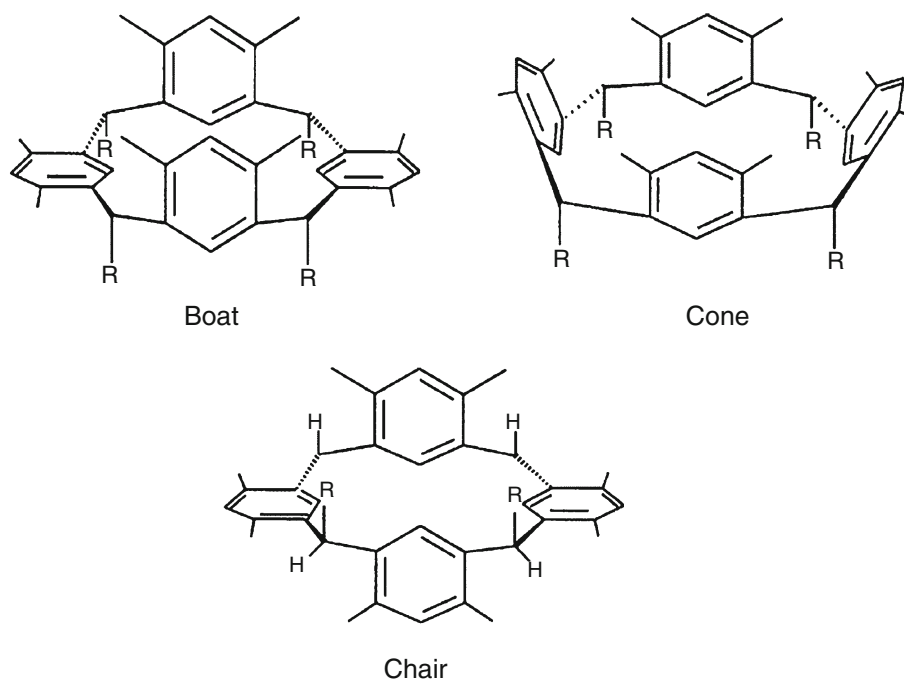

Fig. 2 Different conformations of calix[4]resorcinarene

Boat

Cone

Chair

This research work deals with the synthesis and characterization of three calix[4]resorcinarene molecules, namely: C-dec-9-en-1-ylcalix[4]resorcinarene, C-*trans*-2, *cis*-6-octa-1,5-dien-1-ylcalix[4]resorcinarene and C-nonyl-calix[4]resorcinarene code named as CAL 11U, CAL 9U and CAL 10, respectively. The three synthesized molecules were the subject of characterization by Attenuated total reflectance–Fourier transform infrared (ATR-FTIR), powder X-ray diffraction (XRD) and simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometric evolved gas analysis (MS-EGA). The molecular structures of the compounds were confirmed using nuclear magnetic resonance spectrometry (¹H NMR and ¹³C NMR).

The compound CAL 11U was synthesized by Azoz et al. [48], the compound CAL 10 has also been reported by

Shen et al. [49], and they were characterized using IR, NMR and XRD. To the best of our knowledge, their thermal behavior was never studied and compared to the XRD analysis, while the compound CAL 9U has been synthesized for the first time and presented in this paper.

Experimental

Synthesis of calixresorcinarenes

The basic synthetic route used in our experiments is valid for almost all calix[4]resorcinarenes [48, 49], and the only difference is the aldehyde utilized; for the CAL 11U, we used the undec-9-en-1-yl aldehyde, for the CAL 9U, we utilized the *trans*-2, *cis*-6-nona-1,5-dien-1-yl aldehyde, and
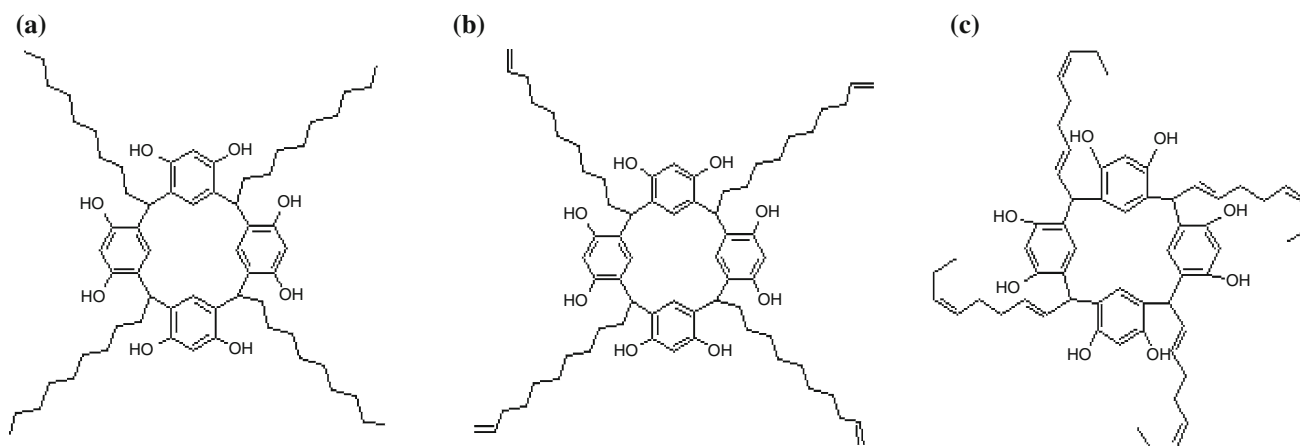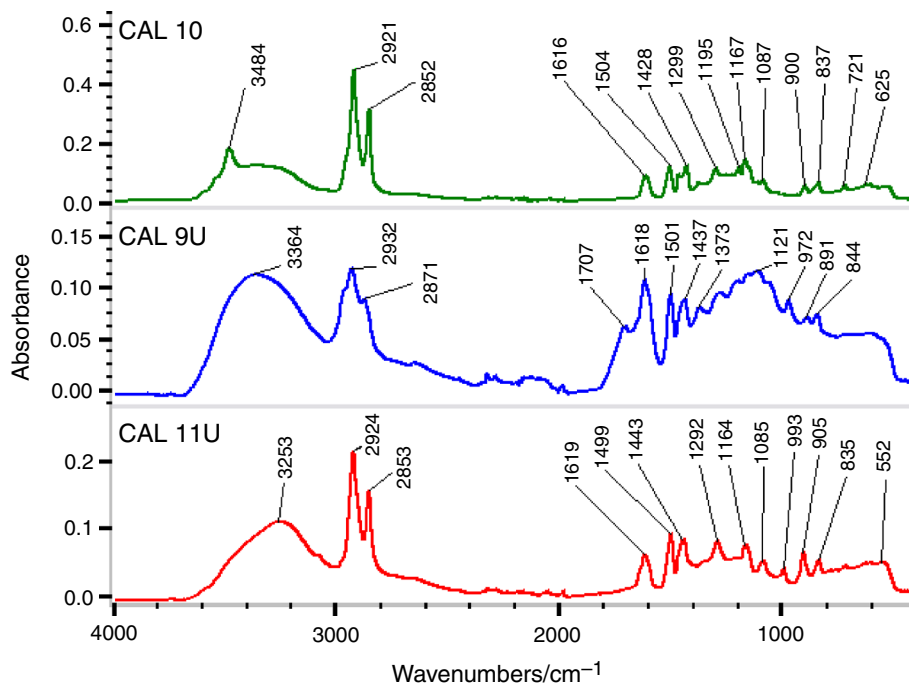
Fig. 3 Molecular structures of the synthesized calix[4]resorcinarenes: **a** C-nonylcalix[4]resorcinarene, **b** C-dec-9-en-1-ylcalix[4]resorcinarene, **c** C-*trans*-2, *cis*-6-octa-1,5-dien-1-ylcalix[4]resorcinarene

Fig. 4 FTIR spectra of the three calix[4]resorcinarenes

for the CAL 10, the decanal has been used; the structures of the three molecules are presented in Fig. 3.

The synthesis was carried out based on the following recipe: 0.23 mol of resorcinol and 0.23 mol of aldehyde were dissolved into 240 mL absolute ethanol. The solution was cooled down to 0 °C in an ice bath, and then 37 mL of concentrated hydrochloric acid was injected, and it was stirred for 1 h, then heated and refluxed for another 12 h. When the mixture was cooled down to room temperature, most of the product precipitated. Excess of water was added to completely precipitate the formed calixresor-cinarene, which was filtered on a glass frit G3 type. The solid material was rinsed by distilled water and dried in vacuum over NaOH or P_2O_5. The recrystallization from methanol and then from an acetone/hexane 1:1 mixture gave a yield of 49%, 50% and 48.8%, respectively, for the compounds CAL 11U, CAL 9U and CAL 10.

FTIR measurements

The IR spectra were collected on a Varian 2000 (Scimitar Series) FTIR spectrometer (Varian Inc., US) equipped with an MCT (mercury–cadmium–telluride) detector and with a single reflection diamond ATR unit (Specac Ltd, UK). The resolution was 4 cm^{-1}. For single spectra, 64 individual

Table 1 IR parameters of the sample 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	=C–H	Stretching	Medium
	3034	=C–H	Stretching	Medium
	1822	C–H	Deformation harmonics	Medium
	1619	C=C	Stretching	Medium
Aromatic	3074	=C–H	Stretching	Medium
	1499	C=C	Stretching	Medium
	1443	C=C	Stretching	Medium
	1980	C–H	Deformation harmonics	Small
	835	C–H	Out plan deformation	Medium to small
Alkane	2924		Asymmetric stretching	Strong
	2853	CH$_2$	Symmetric stretching	Medium
	721		Rocking	Medium to small

Table 2 IR parameters of the sample 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 _Cis_	=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

scans were averaged; all spectra were ATR-corrected by the instrument's data acquisition software (ResPro 4.0).

NMR studies

The NMR measurements were performed at 600 MHz (400 MHz) in DMSO-d6 at 25 °C (40 °C, 50 °C) on Varian VNMR SYSTEM™ spectrometers. An indirect detection triple resonance ^{1}H {^{13}C, X} Z-gradient probe was used. And, the proton and carbon chemical shifts are referenced to the residual solvent signals (δ_{1H} = 2.50 ppm, δ_{13C} = 39.5 ppm).

Thermal analysis

Simultaneous thermogravimetric, differential scanning calorimetric and mass spectrometric (TG–DSC–MS) measurements were performed on a Setaram Labsys Evo thermal analyzer, in helium (6.0) atmosphere, with a flow rate of 90 mL min^{-1}. The heating rate was 20 °C min^{-1}, and 7–8 mg of sample was weighed into 100-µL aluminum

Table 3 IR parameters of the sample CAL 10

Molecule parts	Wave number/cm^{-1}	Bond	Nature of vibration	Intensity
Resorcinol	3484	Associated O–H	Stretching	Strong and 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

crucibles. The measurements were recorded in the 20–500 °C temperature range. The obtained data were baseline-corrected and further evaluated by the thermoanalyzer's processing software (Calisto Processing, ver. 1.492). Parallel with the TG–DSC measurement, the analysis of the evolved gases/decomposition products were carried out on a Pfeiffer Vacuum OmniStarTM Gas Analysis System coupled to the above-described TGA. The gas splitters and transfer lines to the spectrometer were thermostated at 230 °C. The measurements were taken in SEM Bar Graph Cycles acquisition mode, in which the total ion current (TIC), the analog bar graph spectra (for structure determination), and the separate ion current of each scanned individual mass (101 masses) were recorded. The scanned mass interval was 10–111 amu, with a scan speed of 20 ms amu^{-1}, and the spectrometer was operated in electron impact mode.

X-ray powder diffraction

The samples subjected for analysis were in the form of finely grinded powders and suitable amounts were pressed in the diffractometer's sample holder. The powders were characterized by X-ray diffraction using a Philips Powder Diffractometer 1810/3710 with Bragg–Brentano parafocusing geometry, by using monochromatic CuKα ($l = 0.154056$ nm) radiation. The diffractograms were recorded at room temperature in the reflection mode, and the data were collected in a 2θ range from 3° to 77° with a step of 0.04° and exposure time at each point of 1.00 s. The main goal of the measurement was to identify the degree of crystallinity of the samples.

Results and discussion

FTIR spectra

The evaluation of the FTIR spectra can help in the determination and confirmation of the chemical structure of the synthesized calix[4]resorcinarenes. The infrared spectra of the three compounds is shown in Fig. 4, the spectrums were recorded in the wave number range (4000–400 cm^{-1}) to confirm the presence of the functional groups. A stretching frequency was observed at 3253 cm^{-1},3364 cm^{-1},3484 cm^{-1} for CAL 11U, CAL 9U and CAL 10 respectively, it's due to the vibration of the OH groups of the calixresorcinarene macrocycles. The difference between the three spectra can be seen in the fingerprint region (2000–400 cm^{-1}), this difference can be explained by the diversity of the alkyl chains in the macrocycles, thus all the functional groups describing the molecular structures were found on the spectra. The Tables 1–3 for CAL 11U, CAL 9U and CAL 10 respectively presents all the functional groups with their wave numbers and nature of vibrations.

NMR studies

The ^{1}H and ^{13}C NMR spectra of the compounds CAL 10 and CAL 11U are presented in Fig. 5; they show characteristic peaks for the aromatic and the aliphatic carbons and protons, confirming the structures suggested. The NMR spectra of the CAL 9U are not presented, for the reason that the compound is not soluble in the majority of deuterated
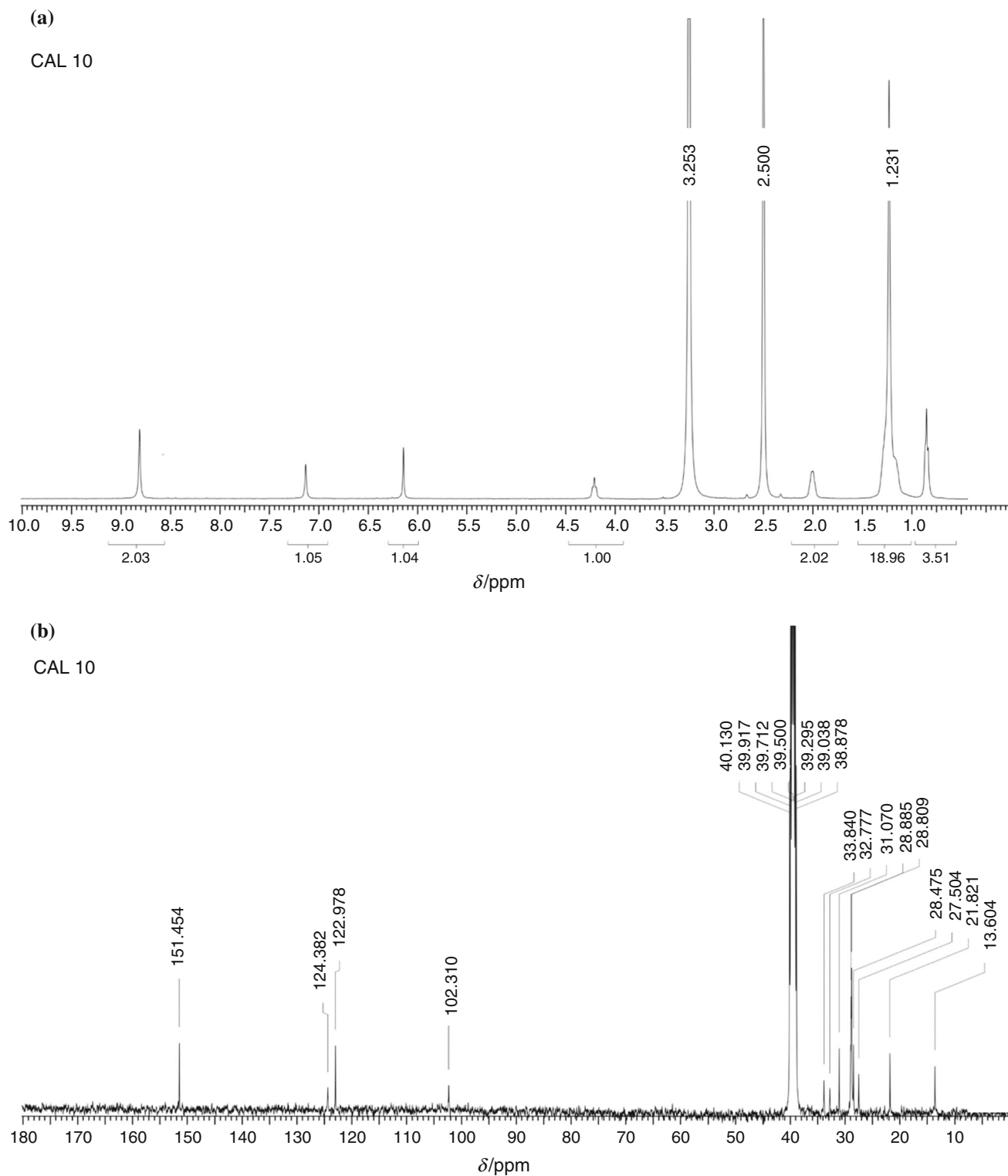
(a)

CAL 10

(b)

CAL 10

Fig. 5 ^{1}H NMR spectra of the compound **a** CAL 10 and **c** CAL 11U, ^{13}C NMR spectra of the compound **b** CAL 10 and **d** CAL 11U

solvents available. The development of a suitable solvent mixture, which could dissolve the calixarene in a suitable concentration for the measurement, is still in process, that is why its NMR spectra will be published in the near future.
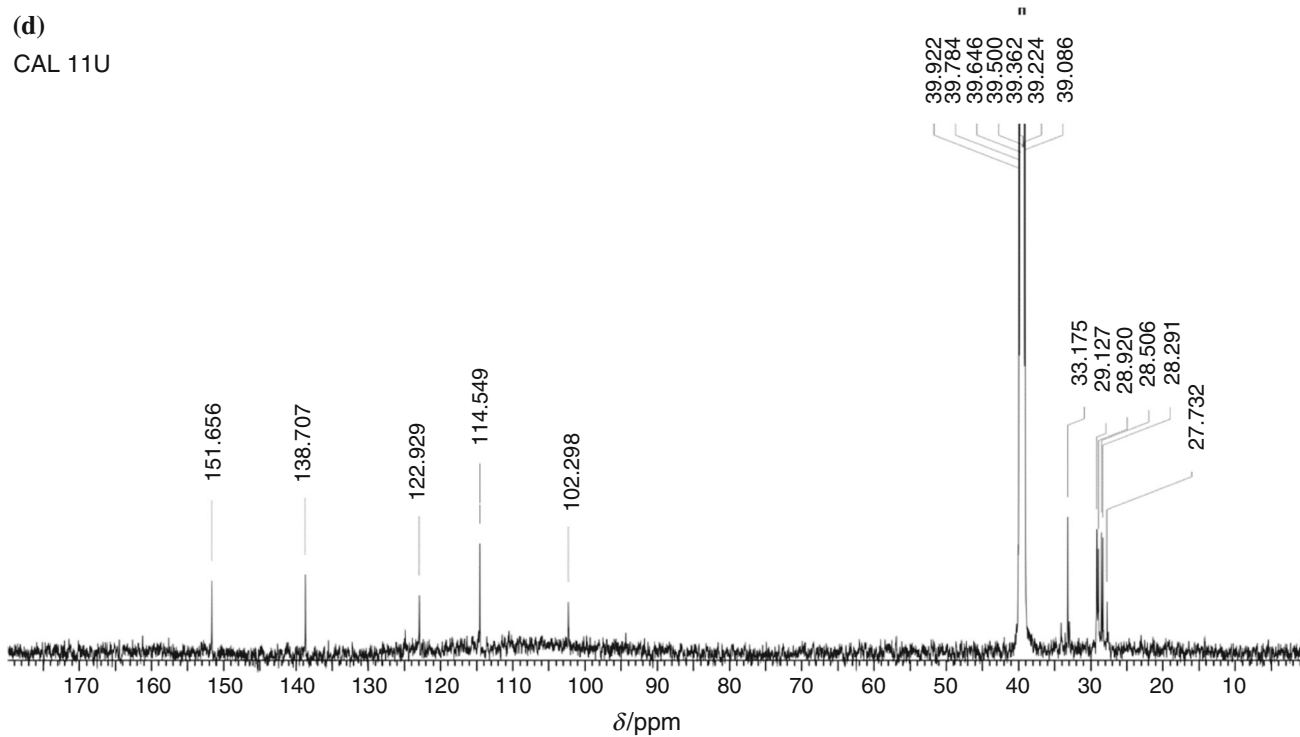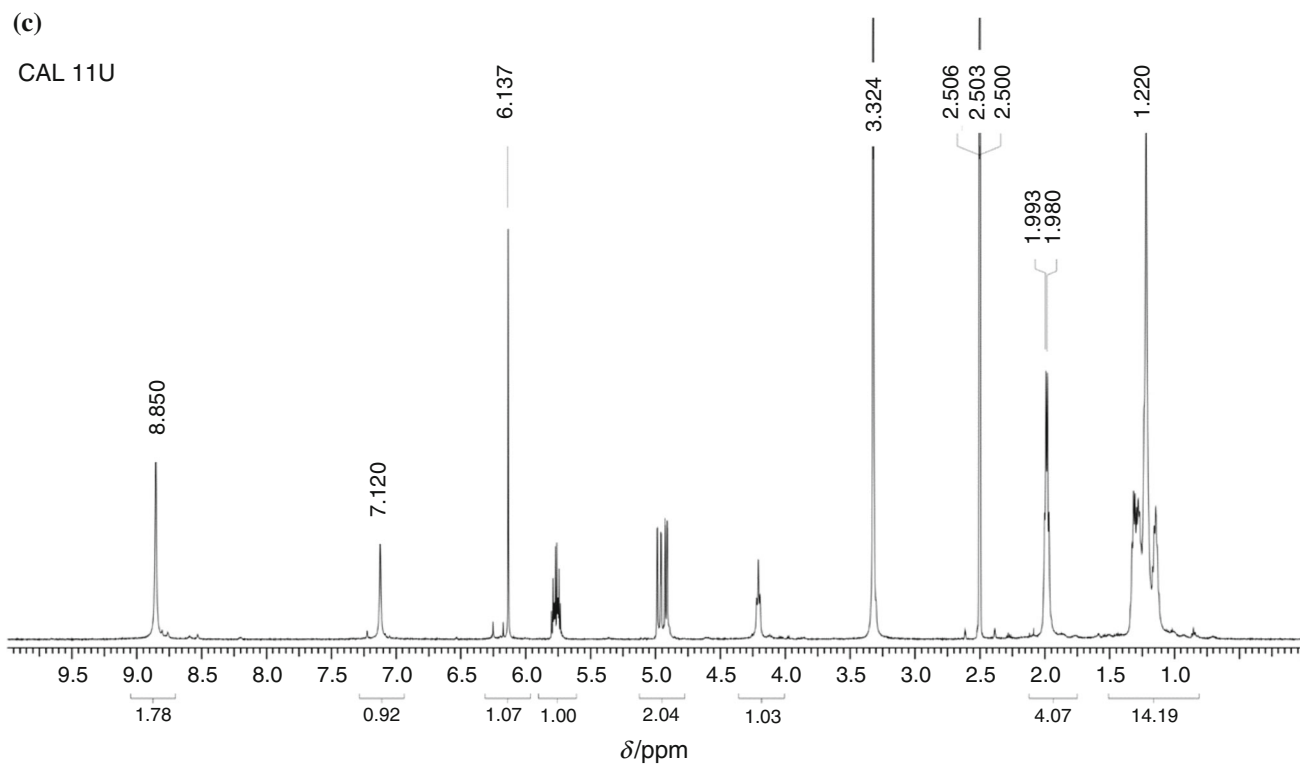
(c)

CAL 11U
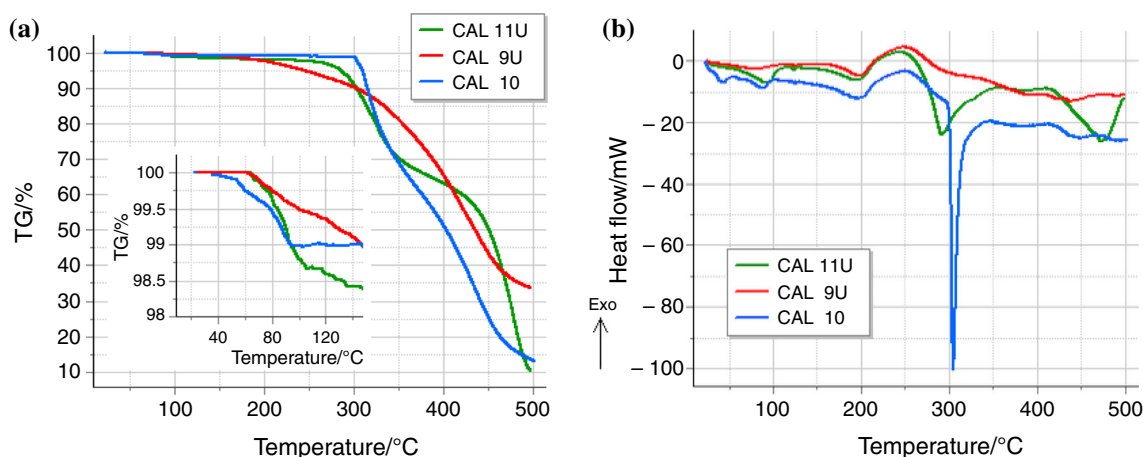

(d)

CAL 11U

Fig. 5 continued

Fig. 6 The results of thermogravimetric (**a**) and differential scanning calorimetric (**b**) measurements (the inset in **a** is a magnification of the TG curve from the beginning of the measurement up to 150 °C)
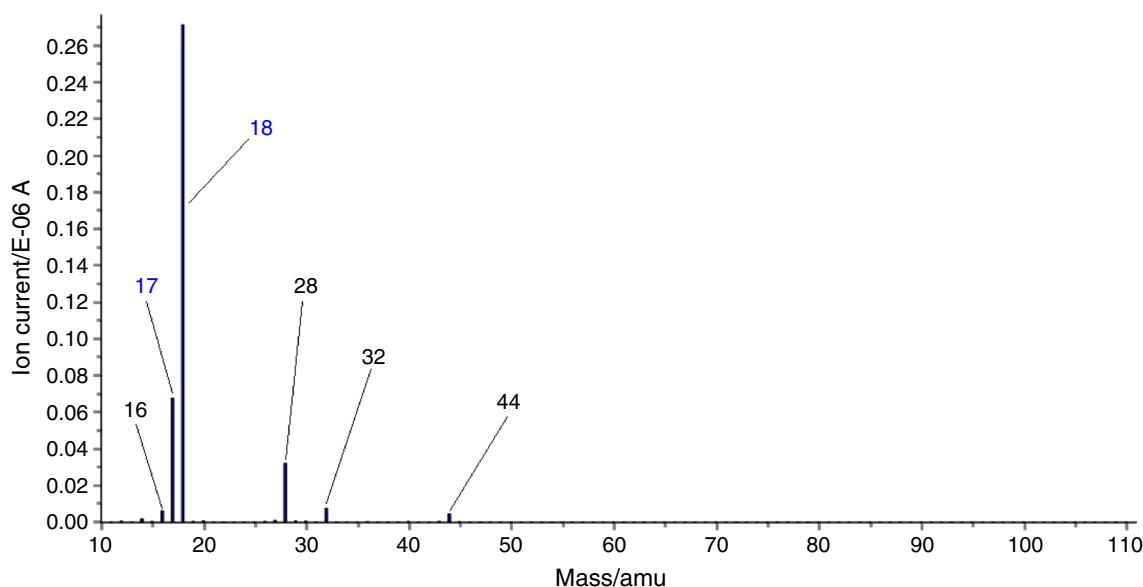

Fig. 7 Mass spectra of the evolved volatiles form sample CAL 10, at 87 °C

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* = 8.0 Hz); 2.02 (8H, *m*); 1.47–1.00 (56H, *m*); 0.82 (12H, *t*, *J* = 6.3 Hz).

^{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* = 8.3 Hz); 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.

Thermal analysis by TG-DSC-MS

The aim of thermal and evolved gas measurements was to determine the thermal stability of the prepared molecules, to measure their melting points and to determine any volatile content released from the samples at lower temperature (determination of any volatile contaminant). In Fig. 6a, the TG curves are plotted against temperature,
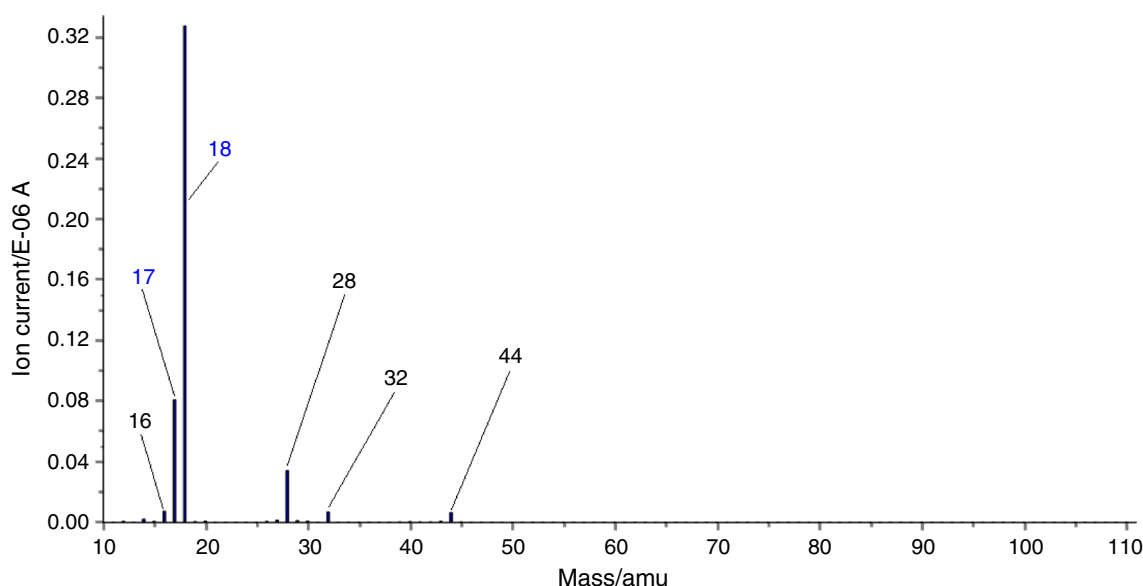
Fig. 8 Mass spectra of the evolved volatiles form sample CAL 9U, at 83 °C

while in Fig. 6b, the corresponding heat flow curves are presented. The inset in Fig. 6a shows a magnified part of the TG curves from the beginning of the measurement up to 145 °C, on which the mass losses at lower temperatures are clearly visible. It can be seen that at lower temperatures (from 40 °C up to 120 °C), a small mass loss step (CAL 11U—1.36%, CAL 9U—0.6% and CAL 10—1.1%) is present on the TG curve of all three investigated samples.

It can also be noticed that the samples are having different thermal stabilities, the less stable is the CAL 9U, which can be explained by its higher degree of unsaturation; each hydrocarbon side chain contains two carbon–carbon double bonds. The degradation of CAL 9U starts above 150 °C and accelerates above 175 °C. In contrary, the CAL 10 is having the highest thermal stability, from 120 °C no mass loss occurs up to 300 °C, above this temperature the calixresorcinarene degrades fast. This outstanding thermal stability can be the consequence of the saturated hydrocarbon side chains in the molecule. Following this idea, the thermal stability of the CAL 11U having one carbon–carbon double bond at the end of the C11 carbon chain should lie in between the two above-mentioned macrocycles, which is also observable in Fig. 6a; the material starts to degrade above 250 °C. The total mass losses determined up to 500 °C are having the following values for each calixarene: CAL 11U—89,76%, CAL 9U—66.34% and CAL 10—86.94%. In Fig. 6b, the heat flow curves of each calixresorcinarene are plotted against temperature. It can be seen that on all three heat flow curves, a small endotherm can be observed around 90 °C, accompanied by small mass losses which are the result of evaporation of physically bound water, or traces of

residual solvents remained from the preparation process. Around 200 °C, a more intensive endothermic transformation is observable on the heat flow curves of all three materials. These endotherms can be the result of some internal molecular transformations in the common calixresorcinarene ring of the molecules, since not all of them are accompanied by mass loss; additionally, the peak maximum values differ only by 2–3 °C (endotherm peak maxima: CAL 11U—194.1 °C, CAL 9U—196.5 °C and CAL 10—196.9 °C). Comparing the heat flow curves of the samples between 250 and 350 °C, a very sharp endotherm can be seen in the case of CAL 10, which corresponds to the melting of the molecule (onset temp. (T_o) 300.75 °C, peak maximum (T_m) 304.23 °C, melting enthalpy (ΔH) 266.7 J g^{-1}). For CAL 11U, in the above-mentioned temperature range, a much smaller and broader endotherm [onset temp. (T_o) 269.5 °C, peak maximum (T_m) 289.9 °C] is noticeable, which is due to the melting of the sample; however, considering the shape of the peak, the calixresorcinarene could be partly crystallized. On the heat flow curve of the CAL 9U, no thermal event is noticeable, which could mean that the sample is amorphous. The events on the heat flow curves above 350 °C are the result of the thermal degradation of the samples.

In Figs. 7–9, the mass spectrometric evolved gas analysis results are presented. The chosen spectra for each investigated compound correspond to the point, where the release of the volatiles takes place at the highest rate (determined using the DTG curve and corrected with the transfer time from the TGA to the mass spectrometer).

In Fig. 7 and 8, the mass spectra of the evolved volatiles formed from sample CAL 10 (at 87 °C) and CAL 9U (at
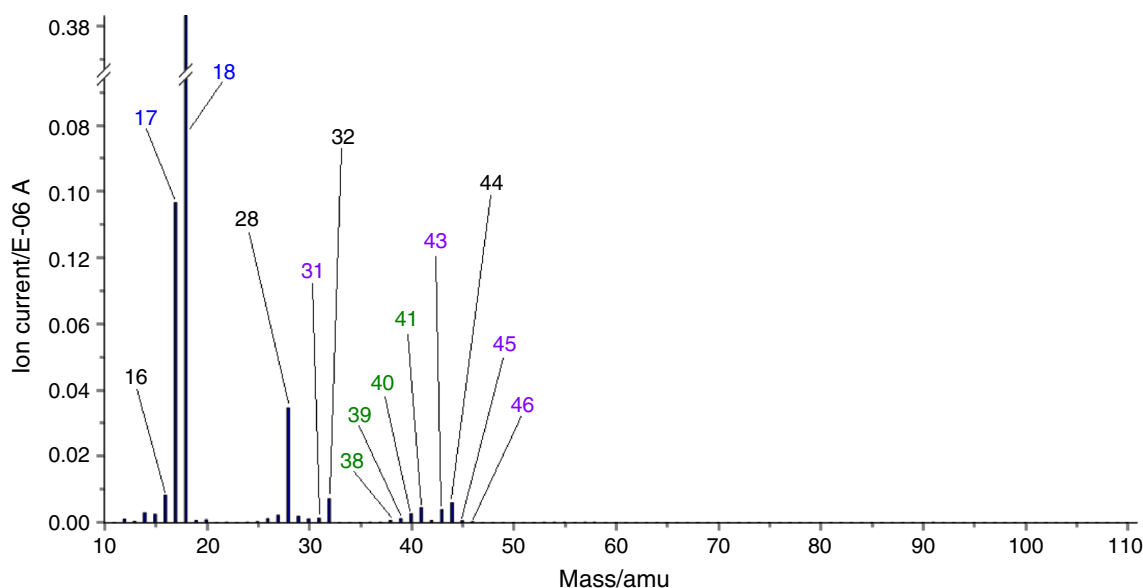
Fig. 9 Mass spectra of the evolved volatiles form sample CAL 11U, at 92 °C

In Fig. 9, the analog mass spectra of the evolved volatiles released from sample CAL 11U (at 92 °C) are plotted. While still the major component formed at 92 °C is water, some traces of acetonitrile (m/z—41, 40, 39 and 38) and ethanol (m/z—46, 45, 43 and 31) can be detected too. These are traces of impurities, which remained in the sample possibly from the preparation and purification processes. The characteristic peaks of the residual air are also visible.

X-ray powder diffraction studies

The aim of the XRD studies was to determine the crystalline or the amorphous character of synthesized calixresorcinarenes. The diffraction patterns of compounds CAL 9U, CAL 10 and CAL 11U are presented in Fig. 10. As it can be seen, the CAL 10 is totally crystalline, the CAL 11U is a mixture of amorphous and crystallized fractions, and the CAL 9U is practically amorphous. By the way, the obtained results are in perfect agreement with the data obtained from the thermal measurements. Based on the XRD patterns, CAL 10 is crystallized; this fact can be observed in the heat flow curve of the sample as a very sharp melting endotherm around 300 °C. CAL 9U is practically amorphous because no thermal event was seen, and CAL 11U is partly crystallized; a small, wide melting endotherm on the heat flow curve confirms this observation.
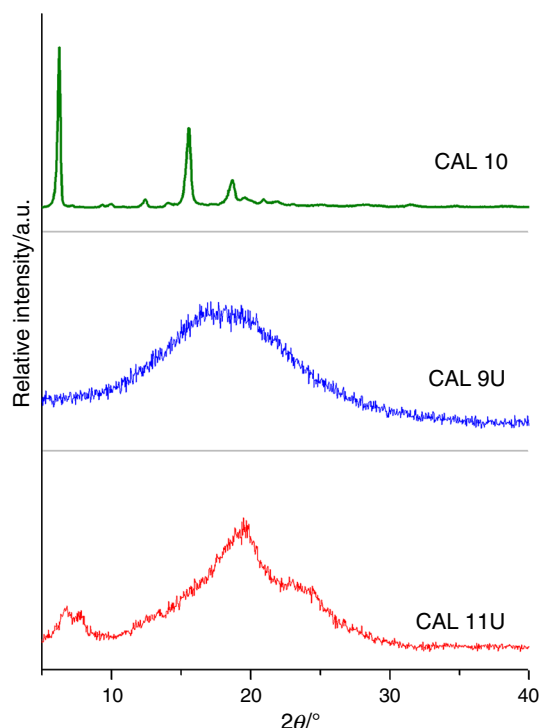

Fig. 10 Powder X-ray diffractograms of the three calix[4]resorcinarenes

83 °C) are shown. On both spectra, the main component is water (m/z—18 and m/z—17), confirming the evaporation of physically bound water. The peaks with m/z—44, 32, 28 and 16—are the characteristic peaks of the components in air, which means that some residual air was still present in the transfer line, which was entrapped during the sample changing process.

Conclusions

A series of three calix[4]resorcinarene macromolecules were synthesized, namely C-dec-9-en-1-ylcalix[4]resorcinarene (CAL 11U), C-*trans*-2, *cis*-6-octa-1,5-dien-1-yl-calix[4]resorcinarene (CAL 9U) and C-nonylcalix[4]resorcinarene (CAL 10); their chemical structure has been confirmed by ^{1}H NMR and ^{13}C NMR studies and ATR-FTIR measurements. The ^{1}H and ^{13}C NMR spectra of the compounds CAL 10 and CAL 11U showed the characteristic peaks for the aromatic and the aliphatic carbons and protons, confirming the structures suggested. Furthermore, the FTIR spectra show similarity in the region between (4000–2000 cm^{-1}), the difference could be seen in the fingerprint region (2000–400 cm^{-1}), and the difference seen is explained by the variance of alkyl chains in the three macrocycles. The thermal behavior of these molecules has been studied by simultaneous thermogravimetry–differential scanning calorimetry coupled to mass spectrometric evolved gas analysis. It has been found that all three investigated samples contain some amount of physically absorbed water and some traces of residual solvents in the case of CAL 11U, which were entrapped by the calixresorcinarenes during their preparation process. The materials are showing different thermal stabilities; the most stable is the molecule having saturated hydrocarbon side chains CAL 10, while the less stable is the one which is having two unsaturated carbon–carbon double bond in the side chain CAL 9U. The crystallized samples are having sharp melting endotherms (the melting point of the samples can be determined). Based on this, they can be differentiated from the amorphous sample CAL 9U. The last step of this study was to evaluate the crystalline character by the X-ray powder diffraction. The CAL 10 is totally crystalline, the CAL 9U is practically amorphous, and the CAL 11U is a mixture of amorphous and crystalline parts. The XRD results were in good agreement with those of thermal analysis.

The synthesis of these macrocycles was the first part of a research project; the second part of this work will be dedicated to the application of these molecules as sensing agents for the detection of toxic metallic elements in the environment by complexation and some electrochemical methods.

References

1. Gutsche CD, Muthukrishnan R. Calixarenes. 1. Analysis of the product mixtures produced by the base-catalyzed condensation of formaldehyde with para-substituted phenols. J Org Chem. 1978;43:4905–6. https://doi.org/10.1021/jo00419a052.

2. Kahlfuss C, Métay E, Duclos M-C, Lemaire M, Oltean M, Milet A, et al. Reversible dimerization of viologen radicals covalently linked to a calixarene platform: experimental and theoretical aspects. C R Chim. 2014;17:505–11. https://doi.org/10.1016/j.crci.2014.01.006.

3. Matvieiev Y, Solovyov A, Shishkina S, Shishkin O, Katz A, Boiko V, et al. Upper-rim calixarene phosphines consisting of multiple lower-rim OH functional groups: synthesis and characterisation. Supramol Chem. 2014;26:825–35. https://doi.org/10.1080/10610278.2014.882511.

4. Pang T-T, Liu H-L, Du L-M, Chang Y-X, Fu Y-L. Supramolecular interaction of two tryptophans with *p*-sulfonated calix [4, 6, 8] arene. J Fluoresc. 2014;24:143–52. https://doi.org/10.1007/s10895-013-1280-0.

5. Espinas J, Pelletier J, Szeto KC, Merle N, Le Roux E, Lucas C, et al. Preparation and characterization of metallacalixarenes anchored to a mesoporous silica SBA-15 LP as potential catalysts. Microporous Mesoporous Mater. 2014;188:77–85. https://doi.org/10.1016/j.micromeso.2013.12.031.

6. Rebarz M, Marcelis L, Menand M, Cornut D, Moucheron C, Jabin I, et al. Revisited photophysics and photochemistry of a Ru-TAP complex using chloride ions and a Calix [6] crypturea. Inorg Chem. 2014;53:2635–44. https://doi.org/10.1021/ic403024z.

7. Liu W, Liu M, Du S, Li Y, Liao W. Bridging cobalt–calixarene subunits into a Co 8 entity or a chain with 4, 4′-bipyridyl. J Mol Struct. 2014;1060:58–62. https://doi.org/10.1016/j.molstruc.2013.12.044.

8. Wang P, Saadioui M, Schmidt C, Böhmer V, Host V, Desreux JF, et al. Dendritic octa-CMPO derivatives of calix [4] arenes. Tetrahedron. 2004;60:2509–15. https://doi.org/10.1016/j.tet.2004.01.057.

9. Dam HH, Reinhoudt DN, Verboom W. Influence of the platform in multicoordinate ligands for actinide partitioning. New J Chem. 2007;31:1620. https://doi.org/10.1039/b603847f.

10. Grimes RN. Chapter 2—structure and bonding. Carboranes. 2nd ed. Oxford: Academic Press; 2011. p. 7–20.

11. Hosmane NS. Boron science: new technologies and applications. Boca Raton: CRC Press; 2011.

12. Mikulášek L, Grüner B, Dordea C, Rudzevich V, Böhmer V, Haddaoui J, et al. tert-Butyl-calix [4] arenes substituted at the narrow rim with cobalt bis (dicarbollide)(1−) and CMPO groups-new and efficient extractants for lanthanides and actinides. Eur J Org Chem. 2007;2007:4772–83.

13. Grűner B, Böhmer V, Dordea C, Seluckỳ P, Bubeníková M. Anionic tert-butyl-calix [4] arenes substituted at the narrow and wide rim by cobalt bis (dicarbollide)(1-) ions and CMPO-groups. Effect of stereochemistry and ratios of the functional groups on the platform on the extraction efficiency for Ln (III)/An (III). J Organomet Chem. 2013;747:155.

14. Persson BR, Holm E. Polonium-210 and lead-210 in the terrestrial environment: a historical review. J Environ Radioact. 2011;102:420–9. https://doi.org/10.1016/j.jenvrad.2011.01.005.

15. Bouvier-Capely C, Bonthonneau JP, Dadache E, Rebiere F. An alternative procedure for uranium analysis in drinking water using AQUALIX columns: application to varied French bottled waters. Talanta. 2014;118:180–5. https://doi.org/10.1016/j.talanta.2013.10.010.

16. Bouvier-Capely C, Manoury A, Legrand A, Bonthonneau JP, Cuenot F, Rebiere F. The use of calix [6] arene molecules for actinides analysis in urine and drinking water: an alternative to current procedures. J Radioanal Nucl Chem. 2009;282:611. https://doi.org/10.1007/s10967-009-0152-1.

17. Adhikari BB, Ohto K, Schramm MP. p-tert-Butylcalix [6] arene hexacarboxylic acid conformational switching and octahedral

18. Ikeda A, Suzuki Y, Yoshimura M, Shinkai S. On the prerequisites for the formation of solution complexes from [60] fullerene and calix [n] arenes: a novel allosteric effect between [60] fullerene and metal cations in calix [n] aryl ester complexes. Tetrahedron. 1998;54:2497–508. https://doi.org/10.1016/S0040-4020(98)00012-X.

19. Adhikari BB, Gurung M, Kawakita H, Ohto K. Cation complexation with p-tert-butylcalix [5] arene pentacarboxylic acid derivative: an allosteric regulation of the first metal ion for stepwise extraction of the second ion. Analyst. 2011;136:3758–69. https://doi.org/10.1039/c1an15199a.

20. Deska M, Dondela B, Sliwa W. Selected applications of calixarene derivatives. Arkivoc. 2015;6(393–41):6. https://doi.org/10.1016/j.msec.2007.10.009.

21. Chiu C-T, Chuang D-M. Molecular actions and therapeutic potential of lithium in preclinical and clinical studies of CNS disorders. Pharmacol Ther. 2010;128:281–304. https://doi.org/10.1016/j.pharmthera.2010.07.006.

22. Gulino A. Structural and electronic characterization of self-assembled molecular nanoarchitectures by X-ray photoelectron spectroscopy. Anal Bioanal Chem. 2013;405:1479–95. https://doi.org/10.1007/s00216-012-6394-8.

23. Ward JP, White JM, Young CG. Synthesis, characterization and metal ion complexation and extraction capabilities of calix [4] arene Schiff base compounds. Tetrahedron. 2013;69:8824–30. https://doi.org/10.1016/j.tet.2013.05.120.

24. Kaya A, Alpoguz HK, Yilmaz A. Application of Cr(VI) transport through the polymer inclusion membrane with a new synthesized calix [4] arene derivative. Ind Eng Chem Res. 2013;52:5428–36. https://doi.org/10.1021/ie303257w.

25. Ni X-L, Jin C-C, Jiang X-K, Takimoto M, Rahman S, Zeng X, et al. Tri-substituted hexahomotrioxacalix [3] arene derivatives bearing imidazole units: synthesis and extraction properties for cations and chromate anions. Org Biomol Chem. 2013;11:5435–42. https://doi.org/10.1039/c3ob40601f.

26. Chen J-H, Hsu K-C, Chang Y-M. Surface modification of hydrophobic resin with tricaprylmethylammonium chloride for the removal of trace hexavalent chromium. Ind Eng Chem Res. 2013;52:11685–94. https://doi.org/10.1021/ie401233r.

27. Sayin S, Ozcan F, Yilmaz M. Two novel calixarene functionalized iron oxide magnetite nanoparticles as a platform for magnetic separation in the liquid–liquid/solid–liquid extraction of oxyanions. Mater Sci Eng, C. 2013;33:2433–9. https://doi.org/10.1016/j.msec.2013.02.004.

28. Kamboh MA, Bhatti AA, Solangi IB, Sherazi STH, Memon S. Adsorption of direct black-38 azo dye on p-tert-butylcalix [6] arene immobilized material. Arab J Chem. 2014;7:125–31. https://doi.org/10.1016/j.arabjc.2013.06.033.

29. Bayrakcı M, Ertul Ş, Yilmaz M. Synthesis of di-substituted calix [4] arene-based receptors for extraction of chromate and arsenate anions. Tetrahedron. 2009;65:7963–8. https://doi.org/10.1016/j.tet.2009.07.062.

30. Zeng J, Guo Q, Ou-Yang Z, Zhou H, Chen H. Chromium (VI) removal from aqueous solutions by polyelectrolyte-enhanced ultrafiltration with polyquaternium. Asia-Pac J Chem Eng. 2014;9:248–55. https://doi.org/10.1002/apj.1764.

31. Sayin S, Eymur S, Yilmaz M. Anion extraction properties of a new "proton-switchable" terpyridin-conjugated calix [4] arene. Ind Eng Chem Res. 2014;53:2396–402. https://doi.org/10.1021/ie4020233.

32. Gulino A, Lupo F, Cristaldi DA, Pappalardo S, Capici C, Gattuso G, et al. A viable route for lithium ion detection. Eur J Inorg Chem. 2014;2014:442–9. https://doi.org/10.1002/ejic.201301213.

33. Cristaldi DA, Fragala I, Pappalardo A, Toscano RM, Ballistreri FP, Tomaselli GA, et al. Sensing of linear alkylammonium ions by a 5-pyrenoylamido-calix [5] arene solution and monolayer using luminescence measurements. J Mater Chem. 2012;22:675–83. https://doi.org/10.1039/c1jm13475b.

34. Ma Y-H, Yuan R, Chai Y-Q, Liu X-L. A new aluminum (III)-selective potentiometric sensor based on N, N′-propanediamide bis (2-salicylideneimine) as a neutral carrier. Mater Sci Eng, C. 2010;30:209–13. https://doi.org/10.1016/j.msec.2009.10.005.

35. Echabaane M, Rouis A, Bonnamour I, Ouada HB. Studies of aluminum (III) ion-selective optical sensor based on a chromogenic calix [4] arene derivative. Spectrochim Acta A Mol Biomol Spectrosc. 2013;115:269–74. https://doi.org/10.1016/j.saa.2013.06.053.

36. Mlika R, Rouis A, Bonnamour I, Ouada HB. Impedance spectroscopic investigation of the effect of thin azo-calix [4] arene film type on the cation sensitivity of the gold electrodes. Mater Sci Eng, C. 2011;31:1466–71. https://doi.org/10.1016/j.msec.2011.05.017.

37. Sun Y, Zhang F, Zhang L, Luo L, Zou Z-L, Cao X-L, et al. Synthesis of calix[4]arene derivatives via a Pd-catalyzed Sonogashira reaction and their recognition properties towards phenols. Chin Chem Lett. 2014;25:226–8. https://doi.org/10.1016/j.cclet.2013.10.019.

38. Düker MH, Schäfer H, Zeller M, Azov VA. Rationally designed calix[4]arene–pyrrolotetrathiafulvalene receptors for electron-deficient neutral guests. J Org Chem. 2013;78:4905–12. https://doi.org/10.1021/jo400502.

39. Pansuriya PB, Parekh HM, Maguire GE, Friedrich HB. Tetramethoxy resorcin [4] arene-tetraester derivatives. J Therm Anal Calorim. 2015;120:653–65. https://doi.org/10.1007/s10973-014-4314-1.

40. Arena G, Pappalardo A, Pappalardo S, Gattuso G, Notti A, Parisi MF, et al. Complexation of biologically active amines by a water-soluble calix [5] arene. J Therm Anal Calorim. 2015;121:1073–9. https://doi.org/10.1007/s10973-015-4522-3.

41. Mokhtari B, Pourabdollah K. Binding mechanisms of nano-baskets toward alkali metals. J Therm Anal Calorim. 2012;110:1043–51. https://doi.org/10.1007/s10973-011-2014-7.

42. Gabdulkhaev MN, Gatiatulin AK, Ziganshin MA, Gorbatchuk VV. Nonlinear effect of two remembered guests in their mixtures on the host memory for guest inclusion and release. J Therm Anal Calorim. 2016;126:627–32. https://doi.org/10.1007/s10973-016-5558-8.

43. Karakuş ÖÖ, Çilgi GK, Deligöz H. Thermal analysis of two series mono-and di-azocalix [4] arene derivatives. J Therm Anal Calorim. 2011;105:341–7. https://doi.org/10.1007/s10973-011-1331-1.

44. Elçin S, Çılgı GK, Karakuş ÖÖ, Deligöz H. A study on thermal behaviors of mono ethyl ester azocalix[4]arene derivatives. J Therm Anal Calorim. 2014;118:719–22. https://doi.org/10.1007/s10973-014-3718-2.

45. Utzig E, Pietraszkiewicz O, Pietraszkiewicz M. Thermal analysis of calix[4]resorcinarene complexes with secondary and tertiary amines. J Therm Anal Calorim. 2004;78:973–80. https://doi.org/10.1007/s10973-005-0463-0.

46. Khabibullin AA, Safina GD, Ziganshin MA, Gorbatchuk VV. Thermal analysis of charge-transfer complex formed by nitrogen dioxide and substituted calix[4]arene. J Therm Anal Calorim. 2012;110:1309–13. https://doi.org/10.1007/s10973-011-2105-5.

47. Saponar A, Popovici E-J, Perhaita I, Nemes G, Cadis A-I. Thermal behaviour of some ester derivatives of p-tert-butyl calix[n]arene. J Therm Anal Calorim. 2012;110:349–56. https://doi.org/10.1007/s10973-012-2415-2.

48. Azov VA, Skinner PJ, Yamakoshi Y, Seiler P, Gramlich V, Diederich F. Functionalized and partially or differentially bridged

resorcin[4]arene cavitands: synthesis and solid-state structures. Helv Chim Acta. 2003;86:3648–70. https://doi.org/10.1002/hlca.200390310.

49. Shen M, Sun Y, Han Y, Yao R, Yan C. Strong deaggregating effect of a novel polyamino resorcinarene surfactant on gold nanoaggregates under microwave irradiation. Langmuir. 2008;24:13161–7. https://doi.org/10.1021/la8019588.