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SILICA GEL MODIFIED WITH FUNCTIONALIZED CALIXARENES. PREPARATION AND CHARACTERIZATION

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ABSTRACT. This work presents the synthesis and characterization of novel products obtained by the chemical bonding of lower rim substituted calix[4]- and calix[8]arene macrocycles to silica gel surfaces modified with aminopropyl chains. The products were investigated by thermogravimetric analysis (DTG, EGA), surface area analysis (BET), as well as by electron microscopy (TEM, SEM).

Keywords: *functionalized silica gel, calixarenes, thermal analyses, electronic microscopy.*

INTRODUCTION

Calix[n]arenes (n = 4 – 20) are phenolic metacyclophanes obtained by the condensation of para- substituted phenol with formaldehyde or para-formaldehyde [1] and they can be functionalized with organic groups by esterification, etherification, sulphonation, nitration or alkylation reactions [2, 3, 4, 5] at the lower rim (the OH phenol groups) or the upper rim (the para position of the phenyl rings). The cavity formed by the phenolic rings and the possibility of functionalizing the calixarenic framework with various organic groups, make these organic macrocycles very interesting for a wide range of applications including biomedical research [6], chromatography [7, 8], selective metal extraction [9, 10], electrochemical and luminescent sensors [11], catalysis [12], and selective gas adsorption [13]. In recent years, more emphasis was put on the immobilization of calixarenes on silica gel substrates, thus improving their possible application in separation sciences [14,15]. One of the most accessible ways to bond calixarene macrocycles to the SiO_2 layer is through alcoxy-silanes of the type $X\text{-}(CH_2)_n\text{-}Si(OR')_3$ [16,17], where X is a functional group that allows coupling reactions with the calixarenic system, usually at the lower rim.

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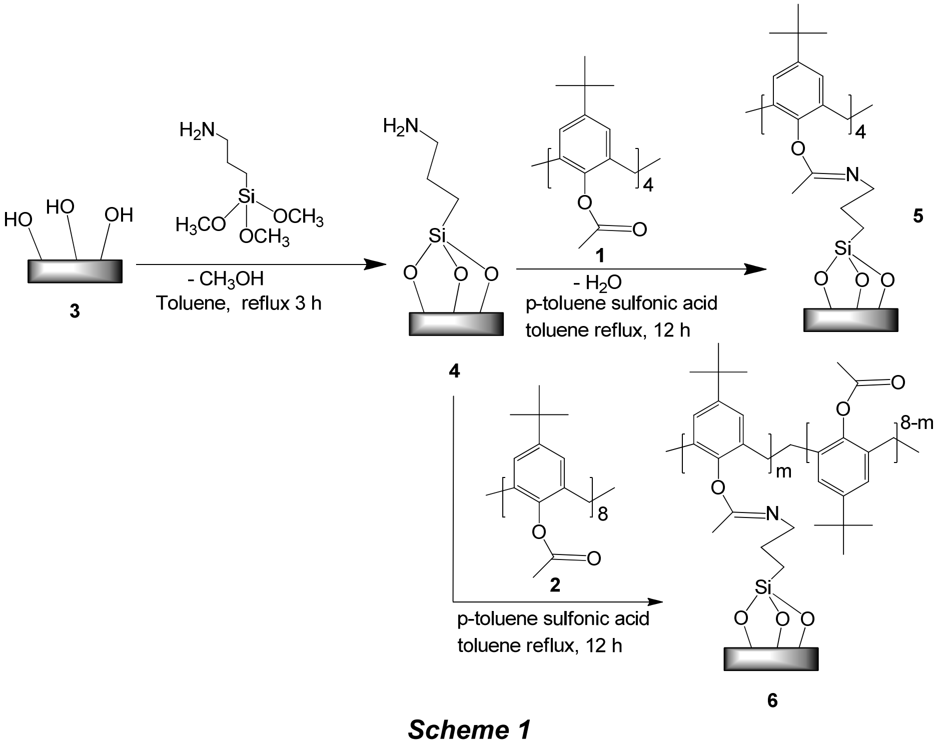
Following this trend, we have studied the preparation of modified silica gel, using 3-aminopropyl-tri-methoxy-silane (APTMS) as a spacer, in order to obtain new products with possible applications in ion metal separation. The reactions were performed in anhydrous conditions by the nucleophilic attack of hydroxyl groups from the silica gel surface at the APTMS spacer, with the elimination of methanol [18].

RESULTS AND DISCUSSION

New modified silica gel with 3-aminopropyl-tri-methoxy-silane (APTMS) and the compound obtained by attaching of this system to the acetylated p-tertbutyl calix[n]arene (n = 4, 8) were synthesized and investigated by specific physico-chemical methods.

A first stage in the synthesis of functionalized calixarenes linked to the silica gel substrate through an aminopropyl spacer requires the preparation of lower rim substituted calixarenes. The starting p-tertbutyl calix[n]arenes (n = 4, 8) and their acetyl derivatives were synthesized according to the methods described in the literature [1,19,20] (Scheme 1, compounds **1**, **2**).



Scheme 1

The APTMS-chemosorbed silica gel **4** was prepared starting from pre-activated silica gel by heating it at 600 °C under reduced pressure (10^{-6} bar) for an hour and products 5 and 6 was performed by a modified literature method [21].

The acetyl functionalized calixarene precursors **1** and **2** were characterized by ^{1}H-NMR and IR spectroscopy, all the obtained data being in agreement with published results [1,19,20]. The new products **5** and **6** were characterized by thermogravimetric methods, surface electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller surface analysis (BET).

The binding of the functionalized calixarenes to the silica surface, with the formation of products **5** and **6** (Scheme 1), was investigated using thermal analysis and electron microscopy (SEM and TEM). The results suggest that the functionalized calixarenic systems **1** and **2** are chemically bonded to the ATPMS modified silica, most likely by means of a C=N bond.

Thermal analysis

Thermal analysis for the new products has been carried out. The thermograms were also recorded for the heat-activated silica gel **3** and the APTMS-modified silica **4**, for comparison. After the treatment of the modified silica **4** with p-tertbutyl calix[4]arene tetra-acetate and the calix[8]arene analogue, the derivative thermogravimetric plots (DTG) differ sharply from those of the calixarene-free materials, as shown in Figure 1 and Table 1.

Table 1. Thermogravimetric analysis data for products 1, 2, 4, 5, and 6.

Product	Quantity (mg)	Thermogravimetric (TG) and (DTG) analysis			
		Total mass loss (Δm_T)	Temperature range	Partial mass loss (Δm_p)	T_{max} (°C)
1	36.5506	86.00 %	25 -260 °C	6.23 %	177
			260 -480 °C	63.48 %	413
			480 -1100 °C	16.30 %	506
2	7.9157	87.26 %	25 -230 °C	4.37%	90
			230 -480 °C	60.12 %	402
			480 -1100 °C	22.81 %	482
4	40.0067	17.15 %	25 -140 °C	3.94 %	70
			140 -800 °C	11.01 %	464
			800 -1100 °C	2.21 %	1008

Product	Quantity (mg)	Thermogravimetric (TG) and (DTG) analysis			
		Total mass loss (Δm_T)	Temperature range	Partial mass loss (Δm_p)	T_{max} (°C)
5	50.8478	36.97 %	25 -160 °C	3.24 %	64
			160 -430 °C	24.51 %	368
			430 -790 °C	7.05 %	458
			790-1100 °C	2.32 %	796
6	26.9450	37.02 %	25 -140 °C	3.39 %	68
			140 -350 °C	17.83 %	279
			350-450 °C	8.83 %	377
			450 – 794 °C	5.18 %	449
			794-1100 °C	1.96 %	815

The thermal analysis data for product **5** indicates that the acetylated p-tertbutyl calix[4]arene is bonded to the silica surface through the APTMS spacer (Figure 1c). The mass loss interval at 160 – 430 °C (24.5 %) is correlated with the elimination of the macrocycle from the system. Another significant mass loss (7 %), between 430 and 600 °C, can be attributed to the decomposition of the aminopropylic chain tethered to the surface.

For derivative **6**, the significantly higher total mass loss (Table 1) indicates the bonding of the organic macrocycles within the new material.

The recorded DTG curve for APTMS-modified silica gel shows a mass loss in the 360-450 °C range, attributed to the decomposition of the APTMS (Figure 1b). The full thermogravimetric data recorded for products **1** – **6** are presented in Table 1.

The comparison of the two DTG recorded for **5** and **6** suggests a stronger bonding of the acetylated calix[4]arene (Figure 1c) on the inorganic surface than in the case of the calix[8]arene analogue (Figure 1d), as the first significant mass loss occurs at higher temperature values for product **5** (Table 1). This can be explained by the preference of calix[4]arenes for a basket geometry, which means that all the acetyl groups in derivative **1** are on the same side of the macrocycle cone [22]. However, larger calixarenes (n = 5, 6, 8), are conformationally mobile, and the cone conformation is almost never preferred. Therefore, it can be assumed that the acetylated calix[8]arene would adopt a conformation allowing fewer connectivity points to the APTMS-modified silica gel via chemical bonding, while physical interactions between the calixarenic unit and the modified substrates are still possible. The coupling of the calix[4]arene to the APTMS-modified silica gel surface through all its connective points can be correlated to the higher decomposition temperature.

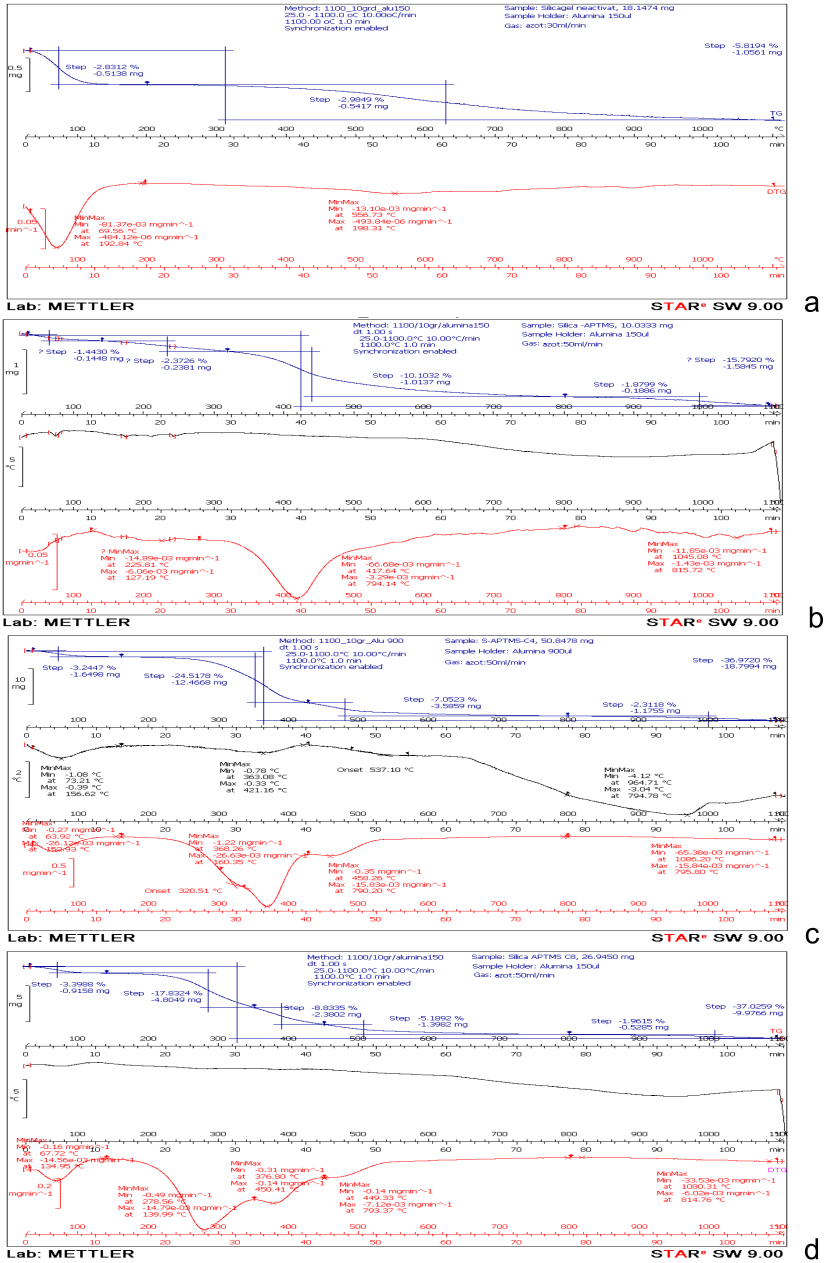
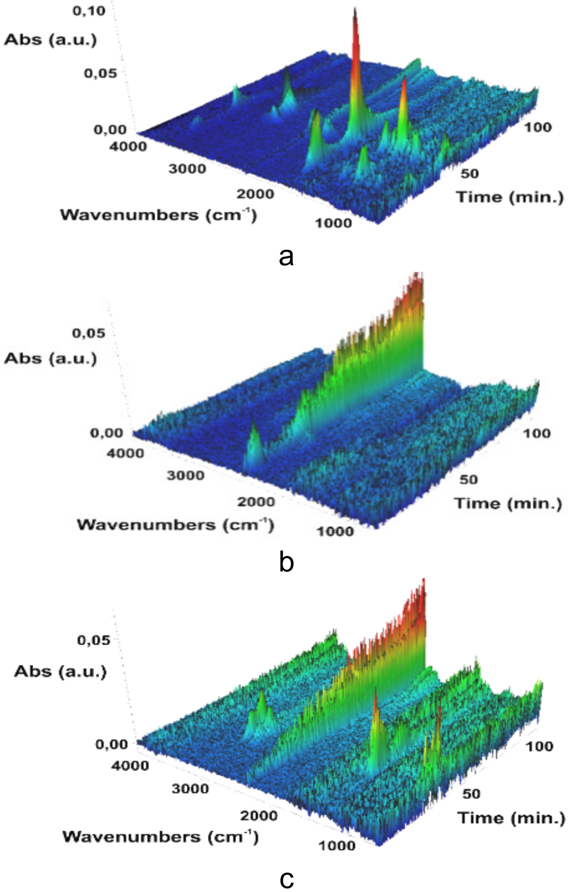


Figure 1. TG and DTG plots for (a) silica gel, (b) APTMS-modified silica gel **4**, (c) silica gel-APTMS-acetyl-p-tertbutyl calix[4]arene **5**, (d) silica gel-APTMS-acetyl-p-tertbutyl calix[8]arene **6**.

Complementary analysis of the new products **5** and **6** by EGA correlates the decomposition of the organic layer to the TG-DTG data. Figure 2 details the recorded EGA data for product **5** (silica gel-APTMS-acetylated calix[4]arene) compared to the starting acetylated calix[4]arene and the APTMS-modified silica gel.



a

b

c

Figure 2. EGA 3D plots for (a) tetra-acetyl derivative of p-tertbutyl calix[4]arene **1**, (b) functionalized silica gel with APTMS **4**, (c) product **5**.

The pattern in the EGA - 3D plot recorded for the decomposition of compound **5** (Figure 2c) indicates the presence of both a calixarene moiety and APTMS fragments, which suggests that the calixarene system is bonded to the inorganic substrate. Similar results were obtained for the calix[8]arene-containing material.

Brunauer–Emmett–Teller surface area analysis

The new products and the starting materials were also investigated through BET surface analysis. As expected, the pore volume of the APTMS functionalized silica gel is much lower than that of the unfunctionalized silica gel due to the covering of the pores with the organic phase (the pore volume decreases from 0.83 cm^3/g to 0.48 cm^3/g). Furthermore, the pore volume in the case of material **5** differs significantly from that obtained for **6**. The larger pore volume of silica gel-APTMS-acetyl-calix[8]arene (0.15 cm^3/g) by comparison with the silica gel-APTMS-acetyl-calix[4]arene system (0.03 cm^3/g) can be explained by a larger cavity of the calix[8] derivative together with a better covering of the silica surfacein the case of **5** (Figure 3).

The pore sizes are relatively small and with a narrow distribution in the meso-porous range (20 - 500 Å). A reduction in pore size was noticed, from an interval of about 50-100 Å determined for the unmodified silica gel to about 35-70 Å for the final product silica gel-APTMS- acetyl calix[8]arene (**6**), (Figure 3). The same pore size interval was determined for the product obtained with the calix[4]arene tetra-acetate (**5**).

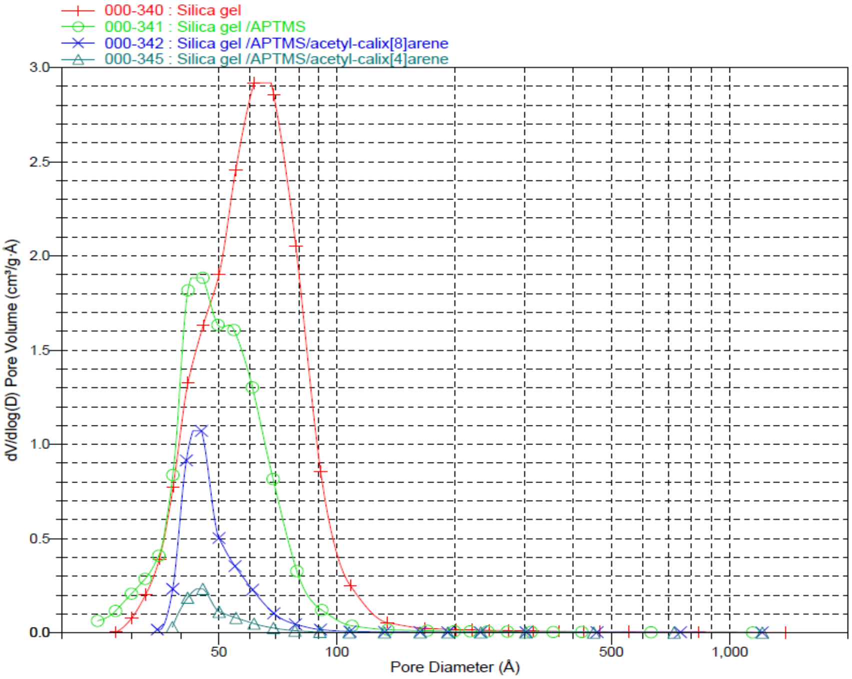


Figure 3. BJH desorbtion pore volume distribution curve according to pore diameter for silica gel (red), silica gel-APTMS **4** (green), silica gel-APTMS-acetyl-calix[4]arene **5** (dark green) and silica gel-APTMS-acetyl-calix[8]arene **6** (blue).

The BET analysis clearly shows that a decrease in pore volume is noticeable after the treatment of the inorganic substrate with APTMS and the calixarene macrocycles, proving that the organic layer covers the silica surface. The BET surface area decreases from 462.20 m^2/g for the silica gel to 301.47 m^2/g for the APTMS modified silica gel and 63.99 m^2/g for product **6** and 11.75 m^2/g for product **5** respectively.

Scanning electron and transmission electron microscopy investigations

SEM images suggest that in both cases the lower rim functionalized calix[n]arenes have been deposited on the APTMS-modified silica gel surface (Figure 4). The images show a relative smooth surface for the unmodified silica gel (Figure 4a), when compared with the products containing either APTMS or the calix[4]arene macrocycle. The APTMS covering of the silica surface does not seem to be uniform (Figure 4b). The same can be told about product **5**, for which the covering of the inorganic substrate is discontinuous. It can be hypothesized that the covering occurred only at the regions on the surfaces already modified with the amino-propyl spacer. By contrast, a smoother surface is observed in the case of product **6**. This, together with the thermal analysis data indicate that the surface is covered uniformly with an organic layer of calix[8]arene.

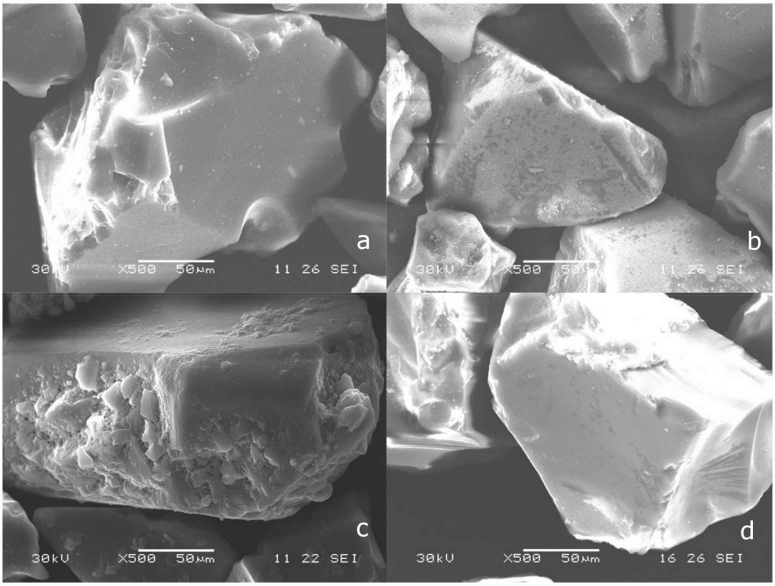


Figure 4. SEM images of (a) silicagel, (b) silica gel-APTMS **4**, (c) silica gel-APTMS-acetyl-calix[4]arene **5** and (d) silica gel-APTMS-acetyl-calix[8]arene **6**.

The new obtained products were also investigated by TEM. Images of the starting activated, unmodified silica gel as well as of the APTMS-modified silica gel are presented for comparison (Figure 5a and b).

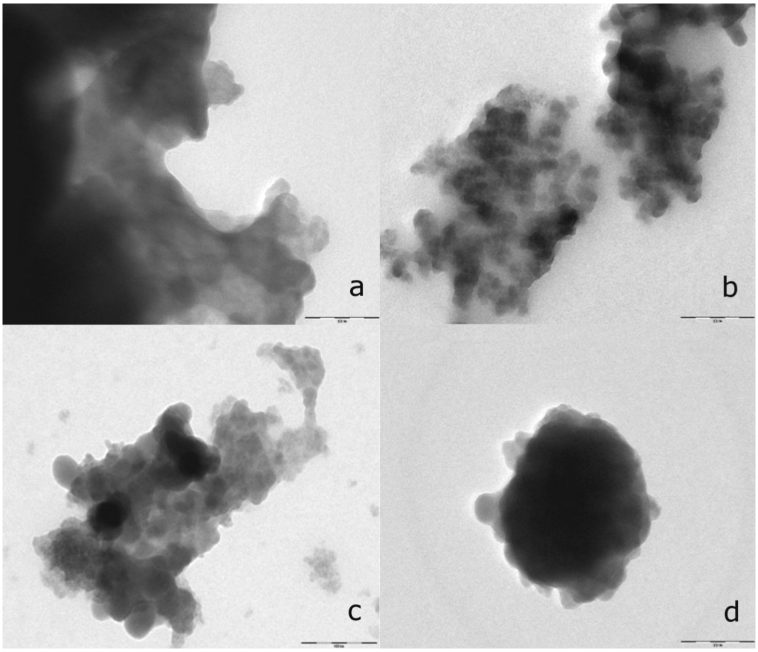


Figure 5. TEM images (Scale: 100 nm) of (a) silica gel, (b) silica gel-APTMS **4**, silica gel-APTMS-acetyl-calix[4]arene **5** and (d) silica gel-APTMS-acetyl-calix[8]arene **6**.

The TEM images of silica gel-APTMS-acetyl-calix[4] arene **5** (Figure 5c) and silica gel-APTMS- acetyl- calix[8]arene **6** (Figure 5d) show that in the case of product **6**, the silica particles aggregate in a higher degree by comparison to the analogue product **5**. This is consistent with the thermogravimetry data suggesting the possibility of calix[8]arene - based material to contain multi-directional bonds of the organic layer to the silica particles while a macrocycle of acetylated calix[4]arene would bond to only one particle.

CONCLUSIONS

This work presents the successful binding of functionalized calix[n]arene (n = 4, 8) derivatives to silica gel by means of 3-aminopropyl trimethoxysilane. The silica substrate was thermally and chemically activated with 3-aminopropyl trimethoxysilane according to literature procedures. The new silica gel-APTMS-acetyl-calix[n]arene systems were characterized by specific methods including DTG, EGA, SEM and TEM, which prove the chemical bonding of the calixarenic macrocycles to the inorganic substrate.

EXPERIMENTAL

All the chemicals were used as purchased from chemical suppliers (Merck, Sigma Aldrich), without any further purification. All reactions have been carried out under argon.

The ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$, with TMS as reference at a frequency of 400.13 MHz.

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851e Thermal Analysis System. All the experiments were done in an alumina crucible (900 µl), with a heating speed of 10°C/min in an interval ranging from 25 to 1100 °C. The measurements were carried out in a nitrogen atmosphere with a flow of 50 ml/min.

The evolved gas analysis (EGA) was performed on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a TG module, operating at 280 °C. Surface area measurements were done on a Tristar II 3020 – Micromeritics (nitrogen adsorption at 77 K, sample decontamination at 150 °C for 24 h, under nitrogen flow).The scanning electron microscopy experiments were performed on a Jeol JSM5510LV (Jeol, Japan) –3.5 nm rezolution, accelerating voltage 0.5-30 kV system. The transmission electron microscopy images were obtained with a Hitachi Automatic TEM H7650 system (accelerating voltage 40-120 kV, zoom 200x-600000x).

Preparation of APTMS-modified silica gel 4. The silica gel was pre-activated by heating it at 600 °C under reduced pressure (10^{-6} bar) for an hour [23]. After the system returned to room temperature, 3-aminopropyl-trimethoxysilane (1.8 mmoles, 0.33 ml) in 20 ml of toluene was added under inert gas and the system was heated to reflux for 3 h. The obtained solid **4** was washed with toluene for 12 h in a Soxhlet extractor.

Synthesis of products 5 and 6. Product **5** was obtained from 2 g of **4**, 0.33 g of **1** and 0.017 g anhydrous p-toluene sulphonic acid in 100 ml of toluene. The mixture was refluxed for 12 h and the resulting solid was then washed with toluene for 12 h in a Soxhlet extractor. Product **6** was obtained in similar conditions from 0.33 g of p-tertbutyl-calix[8]arene octa-acetate **2**.

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