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Conformationally blocked quinoxaline cavitand as solid-phase microextraction coating for the selective detection of BTEX in air

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Abstract

A tetraquinoxaline cavitand functionalized with methylenoxy bridges at the upper rim is proposed as selective solid-phase microextraction (SPME) coating for the determination of BTEX at trace levels in air. The SPME fibers were characterized in terms of film thickness, morphology, thermal stability and extraction capabilities. An average coating thickness of 35 (± 4) μm , a thermal stability up to 400°C and a good fiber-to-fiber and batch-to-batch repeatability with RSD lower than 15% were obtained. Excellent enrichment factors ranging from 360 - 700 $\times 10^3$ were obtained for the investigated compounds. Finally, method validation proved the capabilities of the developed coating for the selective sampling of BTEX, achieving LOD values in the low ng m^{-3} range.

Keywords: Solid-phase microextraction, BTEX, Cavitands, Air monitoring

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1. Introduction

The detection of airborne aromatic hydrocarbons is a long-standing problem due to the need of determining low benzene levels in the presence of overwhelming amounts of water and other hydrocarbons. Pre-concentration is one of the most used approach for BTEX enrichment both in urban and indoor air [1]. The major drawbacks of this approach are related both to the lack of selectivity and to the use of time-consuming procedures like the chemical desorption of the analytes by solvent extraction before analysis.

Most of the approaches implemented so far to solve selectivity problem rely on gas chromatography/mass spectrometry requiring the pre-concentration of the analytes in sorbent traps before separation and determination [2].

Owing to its simplicity, possible automation and low cost, solid-phase microextraction (SPME) [3] is an attractive alternative to most of the conventional sampling technologies. In addition to commercially available devices, different coatings based on carbon nanotubes [4], graphene nanosheets [5], cobalt and zinc oxide nanoparticles [6,7], vinyl-functionalized mesoporous organosilica [8], molecular imprinted polymers (MIP) [9] and different ionic liquids-based materials [10-12] are available for BTEX enrichment in water samples. In this field the exploitation of molecular receptors as sensing materials can be particularly attractive to address the selectivity issue. Through the design, synthesis and characterization of new receptors, innovative highly selective molecules, which are more responsive towards specific host-guest interactions, can be developed. A conformationally mobile tetraquinoxaline-bridged cavitand (QxCav, Chart 1) was already proposed by our research group both as adsorbent material for both dynamic headspace [13] and as SPME coating [14] for the selective sampling of BTEX from water samples, whereas calix[4]arene-based SPME fibers were proposed by Zeng and

coworkers [15]. In addition, different supramolecular receptors like calix[n]arene (n=4, 6, 8)-based Langmuir-Blodgett thin films [16] or allyl substituted γ -cyclodextrin derivatives were used as sensing devices for the real time detection of BTEX [17].

Among BTEX, benzene stands out as carcinogenic agent, being classified in Group 1 by the International Agency for Research on Cancer [18]. Accordingly, the European Commission has set for benzene an exposure limit of $5 \mu\text{g m}^{-3}$ on an average period of one year [19]. Therefore, due to the concurrent requirements of high selectivity and extreme sensitivity, benzene detection in air remains extremely challenging.

To enhance both the selectivity and the sensitivity of BTEX detection, we present a novel SPME coating based on a conformationally rigid cavitand receptor characterized by four methylenoxy connecting units among the quinoxaline bridges (**cavitand 1**, Chart 1). The proposed cavitand is compared to the commonly used commercial fiber coatings in terms of thermal stability, film thickness, enrichment factor and selectivity. Finally, the selective enrichment of BTEX in real-world air samples is demonstrated.

2. Experimental

2.1 Chemicals and Materials

Hydrochloric acid (37%), benzene and ethylbenzene (99.8 and 99.5% purity, respectively) were from Carlo Erba (Milano, Italy). Benzene- d_6 (internal standard, 99.96 atom % D), boron tribromide (BBr_3 , anhydrous), 1,4-dimethoxybenzene, oxalic acid, diethyl ether, n-pentane and n-nonane (all 99% purity), bromochloromethane (50 ppm BHT stabilized), dichloromethane, and N,N-dimethylacetamide (DMA) (all 99.5% purity), 1,2-dichloroethane and N,N-

dimethylformamide (DMF) (both 99.8% purity), ethanol, methanol and toluene (all 99.9% purity), heptaldehyde (95% purity), nitric acid 65%, n-hexane (97% purity), n-octane (98% purity), palladium on carbon catalizer (Pd/C cat, 10% w/w), phosphorus oxychloride (POCl₃, 99% purity) were from Sigma-Aldrich (Milan, Italy). n-Heptane (95% purity) was provided by Lab-Scan (Dublin, Ireland), whereas aluminum chloride (AlCl₃, anhydrous, crystallized, ≥ 99 % purity), *m*-xylene, *p*- and *o*-xylene (all 98% purity) were from Fluka (Milan, Italy).

SPME bare fused-silica fibers and commercial fibers 75 μ m Carboxen-PDMS (CAR-PDMS) and 2cm-50/30 μ m PDMS-Carboxen-DVB (PDMS-CAR-DVB) were purchased from Supelco (Bellefonte, PA, USA). Duralco 4460 epoxy glue was provided by Cotronics Corp. (Brooklyn, NY, USA). 1L Tedlar[®] Gas Sampling Bags w/PLV and Thermogreen[®] LB-2 Septa were from Sigma-Aldrich.

2.2 Cavitand synthesis

The detailed synthesis of **cavitand 1** is reported in the Supplementary Data (Schemes S1-S2).

2.3 Fiber preparation

The fiber coating was obtained by vertically dipping the silica support of the fiber in the Duralco 4460 epoxy glue and, after 2 min, in the cavitand powder for three times. Four fibers were prepared and tested.

2.4. Structural determination and fiber characterization

Intensity data and cell parameters for benzene@cavitand were recorded at 190 K on a Bruker APEX II equipped with a CCD area detector and a graphite monochromator (MoK α radiation $\lambda =$

0.71073 Å). The structure was solved by direct methods using the SIR97 program [20] and refined on F_o^2 by full-matrix least-squares procedures using the SHELXL-97 program [21,22]. Both programs were used in the WinGX suite [23]. Data reductions were performed using the SAINT [24] and SADABS [25,26] programs. The PLATON SQUEEZE procedure [27] was used to treat regions of diffuse solvent which could not be sensibly modeled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified F_o^2 written to a new HKL file and the number of electrons located were included in the formula, formula weight, calculated density, μ and F(000). The residual electron density was found to be of 122 electrons per unit cell and was assigned to two chloroform molecules. All the non-hydrogen atoms were refined with anisotropic atomic displacements, with the exclusion of some atoms of a disordered alkyl chains at the lower rim. The hydrogen atoms were included in the refinement at idealized geometries (C–H 0.95 Å) and refined “riding” on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.0911P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Geometric calculations were performed with the PARST97 program [28]. Crystallographic data and refinement details for benzene@cavitand are reported in Supplementary Data (Table S1).

^1H NMR spectra were recorded both on Bruker Avance 300 (300 MHz) and on Bruker Avance 400 (400 MHz) spectrometers (Bruker Italia, Milan, Italy). Chemical shifts are reported in parts per million (ppm) referenced to that of residual solvent protons. Acetone- d_6 , dichloromethane- d_6 , and dimethyl sulfoxide- d_6 were used as solvents.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Waters ACQUITY UPLC® SQ Detector (Waters S.p.a., Milano, Italy).

Matrix-assisted laser desorption/ionization time-of-flight tandem mass spectrometry (MALDI TOF-TOF-MS) was performed on AB SCIEX MALDI TOF-TOF 4800 Plus instrument (AB Sciex S.R.L., Brugherio (MB), Italy) using α -Cyano-4-hydroxycinnamic acid as a matrix.

Thermogravimetric analysis (TGA) was performed using a TGA 7 instrument (Perkin-Elmer, Waltham, MA) over the temperature range 40-400°C (heating rate: 10°C min⁻¹) under inert (N₂) atmosphere. Coating thickness and surface morphology were investigated by using scanning electron microscopy (SEM) with a Leica 430i instrument (Leica, Solms, Germany). Fiber bleeding was investigated by desorbing the fibers in the GC injection port for 2 min at 250°C. Fiber-to-fiber and batch-to-batch repeatability were evaluated for headspace analysis by using four fibers in each case. Three replicated measurements for each fiber were always performed.

2.5. SPME Analysis

Prior to use, all the fibers were conditioned in the GC injection port at 275°C for 1 h under a helium flow. Air sampling of BTEX was performed by manually exposing the SPME fibers in an air atmosphere containing a mixture of the aromatic compounds and linear hydrocarbons (from C₆ to C₉). Extraction was carried out at room temperature for 15 min. The same procedure was applied using the commercial fibers, 75µm CAR-PDMS and 2cm-50/30µm PDMS-CAR-DVB (Supelco).

2.6 GC/MS analysis

A HP 6890 Series Plus gas chromatograph (Agilent Technologies, Palo Alto, CA) equipped with a MSD 5973 mass spectrometer (Agilent Technologies) was used. Helium was used as the carrier gas at a constant flow rate of 1 mL min⁻¹; the gas chromatograph was operated in splitless mode

for 1 min with the PTV injector (Agilent Technologies) maintained at the temperature of 250°C and equipped with a 1.5 mm i.d. multibaffled liner (Agilent Technologies). Chromatographic separation was performed on a 30 m x 0.25 mm, df 0.25 µm HP-5 ms capillary column (Agilent Technologies), using the following temperature programme: 40°C for 8 minutes, then 20°C min⁻¹ up to 200°C.

The transfer line and source were maintained at the temperatures of 220 and 150 °C, respectively. Preliminarily, full scan EI data were acquired to determine appropriate masses for selected-ion monitoring mode (m/z 78 and 84 for benzene and d₆-benzene; m/z 91 for toluene; m/z 91 and 106 m/z for ethylbenzene and xylenes; m/z 43, 57, 72 and 86 for hexane; m/z 43, 57, 71 and 100 for heptane; m/z 43, 57, 85 and 114 for octane; m/z 43, 57, 85 and 128 for nonane) under the following conditions: ionization energy: 70 eV; mass range: 35-250 amu; scan time: 3 scan s⁻¹; electron multiplier voltage: 2200 V. Signal acquisition and data handling were performed using the HP Chemstation (Agilent Technologies).

2.7 Method validation

Method validation was performed according to EURACHEM guidelines [29] following the same procedure reported in previous studies [30].

2.8 Real samples

Two air samples were collected on December, at two different times (9:00 and 16:00), by using 1L Tedlar[®] Gas Sampling Bag w/PLV and Thermogreen[®] LB-2 Septa (Sigma-Aldrich) in a traffic busy street in Parma, Italy. SPME analysis was then performed for 15 min at room temperature.

3. Results and discussion

3.1 Design and synthesis of cavitand 1

With respect to the already reported class of QxCav used for benzene detection [14,31,32], in this study we introduce a novel cavitand characterized at the upper rim by the presence of four methylenoxy connecting units among the quinoxaline bridges. The cavitand was designed in order to achieve the highest selectivity and sensitivity for benzene detection; to this purpose, the following goals were addressed: (i) freeze the conformational mobility of the QxCav [33,34] in order to strengthen the complexation of aromatic guests (sensitivity gain); (ii) reduce the cavity opening at the upper rim to hamper the uptake of substituted aromatic compounds (selectivity gain).

The three-step synthesis of cavitand **1** is described in detail in the SI (Scheme S2); it starts with the fourfold bridging reaction of the hexyl-footed resorcinarene under basic conditions with 2,3-dichloro-5,8-dimethoxy quinoxaline (**4**) to form the octamethoxy-quinoxaline cavitand (**5**), which was successively reacted with AlCl₃ in dry toluene to cleave the methyl protecting groups of the quinoxaline walls (cavitand **6**). The final bridging step is the critical one, due to the high strain of the final product. Reaction of **6** with an excess of chlorobromomethane under basic conditions led to the formation of the desired **1** in just 5% isolated yield. Although several reaction conditions were tested (solvent, temperature, reaction times and pressure), no significant improvements in the yield of the final step were obtained. The high strain experienced by the methyedioxy bridges is reflected in the difficulty of their arrangement.

3.2 Crystal structure of the complex

The molecular structure of benzene@cavitand, is shown in Fig. 1. The host-guest complex was obtained from a chloroform solution containing benzene. Due to the presence of short bridging groups at the upper rim, the overall structure is highly strained, the quinoxaline units are blocked conformationally and the available space for the guest is reduced with respect to the parent QxCav. The cavity has a depth of 8.063(2) Å and the opening of the cavity is rhombohedral with dimensions of about 8 and 12 Å). Benzene perfectly fits the inner volume of the cavity, stabilized by C-H $\cdots\pi$ interactions between the guest hydrogen atoms and two aromatic rings of the receptor [C_{guest} \cdots centroid distances are 3.717(3) and 3.766(3) Å; C-H \cdots centroid angles are 146.72(2) and 156.17(4)°]. The inward facing hydrogen atoms of the methylenedioxy bridges further stabilize the benzene guest molecule through the formation of van der Waals interactions. They are conformationally blocked not only in the solid state but also in solution, as proven by their different chemical shift in the ¹H NMR spectrum (Fig. S1)

3.3 Cavitand-coated fiber characterization

The thermal stability of **cavitand 1** was assessed by means of TGA (Fig. S2). An excellent stability was demonstrated, the cavitand being stable up to 400°C: with respect to the parent QxCav [14], the presence of the four methylenedioxy bridges did not reduce the thermal stability of the modified receptor. The thermal stability of the coating was also evaluated by conditioning the SPME fibers in the GC injector port at 250°C for 2 minutes: no significant bleeding was observed, thus confirming the high thermal resistance of the material.

The morphology of the coated fibers was investigated by scanning electron microscopy under different magnifications (Fig. 2), revealing a homogeneous and uniform coating on the entire surface of the fiber. The average thickness of coating was found to be $35\pm 4\ \mu\text{m}$ ($n=3$).

The performance of the developed adsorbent material was assessed both in terms of fiber-to-fiber and batch-to-batch repeatability obtaining RSD always lower than 15% also when sampling was performed along different days.

3.4 Selectivity studies

The BTEX enrichment properties of cavitand-coated fiber were tested by sampling an air mixture containing BTEX and aliphatic hydrocarbons in the $385\text{-}473\ \text{ng m}^{-3}$ and $38\text{-}56\ \mu\text{g m}^{-3}$ range for BTEX and aliphatic hydrocarbons (from C_6 to C_9), respectively. Consecutive desorption experiments at different temperatures showed that aliphatic hydrocarbons can be completely desorbed between 50 and 100°C , whereas BTEX desorption begins at 200°C and is exhaustive only at 250°C . This striking gap in desorption temperature reflects the different binding mode of the two classes of analytes: BTEX are complexed by **cavitand 1** in the cavity, whereas aliphatic hydrocarbons are physisorbed by the organic coating.

The preferential adsorption of BTEX was also evaluated in terms of enrichment factors (EFs) [35]. EFs were calculated as the ratio of the concentration of the analyte in the fiber after the extraction to that of the analyte in the gas standard mixture (i.e. using the ratio of the chromatographic peak area of the analyte after SPME to that before extraction obtained by the direct injection of the same gas standard solution, $n=3$). The EFs were calculated for each analyte: benzene ($700\pm 51 \times 10^3$), toluene ($410\pm 26 \times 10^3$), ethylbenzene ($550\pm 45 \times 10^3$), *m*-xylene ($360\pm 30 \times 10^3$), *p*-xylene ($570\pm 35 \times 10^3$) and *o*-xylene ($360\pm 25 \times 10^3$).

The highest EF was observed for benzene, thus proving that the steric hindrance affects the selectivity in analyte inclusion. The presence of the methylenedioxy bridges reduces the cavity opening, thus facilitating the entrance of benzene with respect to the other aromatic analytes.

Finally, a comparison among the enrichment capabilities of the cavitand coating and commercially available adsorbent SPME fibers (75 μ m CAR-PDMS and 2cm-50/30 μ m PDMS-CAR-DVB) was carried out. As reported in Fig. 3, the cavitand-coated fiber extracted up to 42 times as much analytes compared to the commercial ones.

3.5 Method validation

Method validation proved the capabilities of the cavitand adsorbent material for the determination of BTEX in air at trace levels. Excellent results with LOD values at the low ng m⁻³ level were achieved for all the target compounds (Table 1). Good linearity was also proved for all the analytes by applying Mandel's fitting test.

Method precision was assessed testing two concentration levels, i.e. 35 and 350 ng m⁻³ for benzene, 40-400 ng m⁻³ for toluene, 47-470 ng m⁻³ for ethylbenzene, *m*-, *p*- and *o*-xylenes. Good results were obtained both in terms of intraday repeatability and intermediate precision, with RSD values always lower than 10%. In the case of intermediate precision, ANOVA showed that mean values were not significantly different among the 3 days, obtaining *p* values > 0.05. Extraction recoveries ranging from 99 \pm 1% to 109 \pm 1% (n=3) were calculated at 24 and 240 ng m⁻³ for all the analytes, showing the good efficiency of the devised method in terms of extraction recovery.

Table 2 shows the comparison among the LOD values obtained by using the **cavitand 1** fiber, the QxCav fiber (used as reference) and other methods proposed for BTEX detection [36,37].

As reported, very low detection limits were achieved by using the **cavitand 1**-coated SPME fiber obtaining LOD values at least one order of magnitude lower than those achieved with the QxCav-coated fiber.

As final test, the developed SPME fiber was applied for the analysis of two real air samples taken, at different times, near an urban traffic fixed-site air monitoring station: the concentration values found i.e. benzene $2.7 \mu\text{g m}^{-3}$, toluene $7.7 \mu\text{g m}^{-3}$, ethylbenzene $1.5 \mu\text{g m}^{-3}$ and xylenes $7.6 \mu\text{g m}^{-3}$ and benzene $2.1 \mu\text{g m}^{-3}$, toluene $6.0 \mu\text{g m}^{-3}$, ethylbenzene $0.9 \mu\text{g m}^{-3}$ and xylenes $4.8 \mu\text{g m}^{-3}$ at 09:00 and 16:00, respectively, were in agreement with those obtained by the on-line measurements performed by the fixed-site station, thus proving reliability of the SPME-GC-MS method for the determination of BTEX in air.

4. Conclusions

A new SPME coating based on **cavitand 1** was developed and tested for the selective and ultrasensitive determination of BTEX in air. With respect to previously developed QxCav SPME fiber, the receptor conformational rigidity and the reduction of the cavity opening allowed to obtain higher enrichment factors, very low detection limits and increased selectivity toward benzene. The main features of the developed material are excellent thermal stability, a very good repeatability and a very good sensitivity with responses up to more than forty-fold higher than those obtained using commercial devices.

Taking into account that this new SPME fiber is insensitive to the most common interfering agents present in air, i.e. aliphatic hydrocarbons, water and other polluting gases like CO, SO_x, NO_x, it can be exploited for the development of portable devices in which **cavitand 1** is used as trapping material for the on-line and *in-situ* environmental monitoring of BTEX.

In addition, BTEX adsorption can be performed in a very short time, thus allowing the use of the proposed SPME fiber for the assessment of short-term exposure in workers.

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Table 1. LOD, LOQ and linearity of the SPME-GC-MS method

	LOD (ng m ⁻³)	LOQ (ng m ⁻³)	Linearity range (ng m ⁻³)	a *	b **
benzene	0.4	1.3	3.5-350	207±2	-
toluene	0.6	1.1	4.1-410	1461±27	-
ethylbenzene	0.5	1.4	4.7-470	1560±45	-
<i>m</i> -xylene	1.2	2.9	4.7-470	421±2	-
<i>p</i> -xylene	0.6	1.4	4.7-470	1760±47	-
<i>o</i> -xylene	1.0	2.5	4.7-470	346±1	-

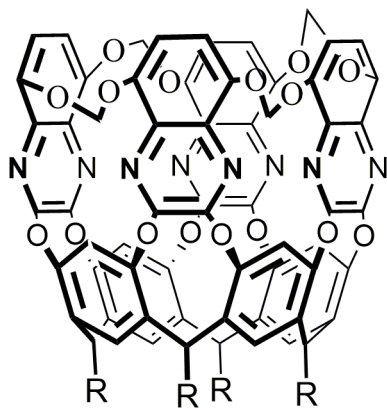
*Regression equation: $y=ax+b$

** Not significant

Table 2. LOD values obtained by using the **cavitand 1** fiber vs LOD values reported in literature.

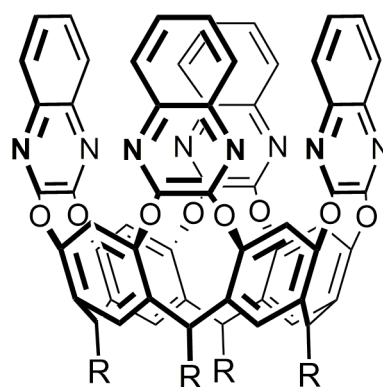
	Cavitand 1	4QxCav	RADIELLOTM[36]	Optical fibre [37]
	(ng m ⁻³)	(ng m ⁻³)	(ng m ⁻³)	(ng m ⁻³)
	15 min [*]	15 min [*]	24 h [*]	25 min [*]
benzene	0.4	5.2	290	1.6
toluene	0.6	7.2	90	1.5
ethylbenzene	0.5	5.7	40	1.2
<i>m</i> -xylene	1.2	10	70	1.3
<i>p</i> -xylene	0.6	9.0	80	1.7
<i>o</i> -xylene	1.0	12.5	10	2.0

^{*} Extraction time used in each study



1

R=C₆H₁₃



QXCav

Chart 1

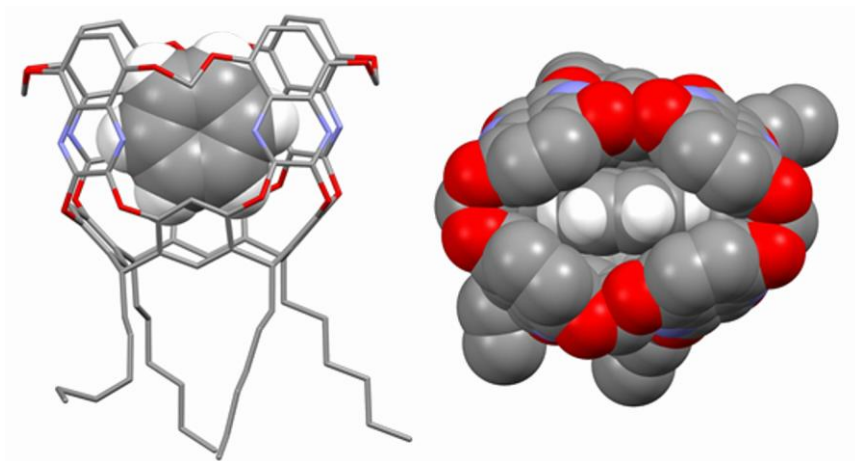


Figure 1

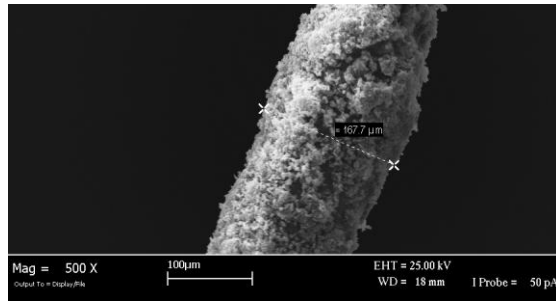


Figure 2

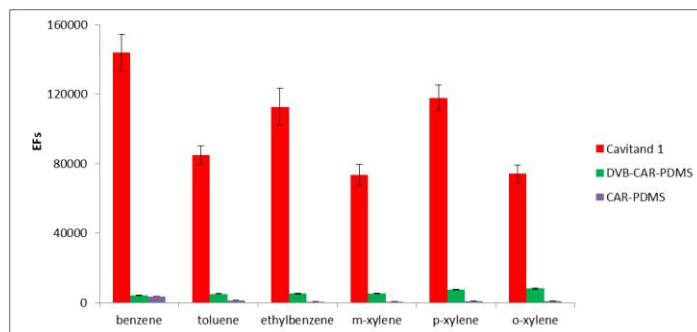


Figure 3

Figure captions

Fig. 1. Left: molecular structure of the **cavitand 1**@benzene complex crystallized from chloroform. The guest is shown in space filling mode. Right: top view of the complex in space filling mode. The hydrogen atoms of the receptor and lattice solvent molecules have been omitted for clarity

Fig. 2. Scanning electron microscope image of the **cavitand 1** fiber. Magnification 500x.

Fig. 3. Enhancement factors per coating thickness of the cavitand-based *vs* commercial coatings for BTEX extraction. Headspace-SPME conditions. Extraction time: 15 min, RT (n=3).