Cavitands as superior sorbents for benzene detection at trace level†

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We present an innovative dynamic headspace-based approach to sampling of BTX using molecular receptors. For this purpose methylene-bridged (MeCav) and quinoxaline-bridged (QxCav) cavitands were silylated at the lower rim and grafted onto silica gel. In the case of QxCav, the resulting sorbent material selectively retains BTX at ppb levels in the adsorption phase and delivers a benzene-enriched fraction in the desorption phase. Under the same conditions, commercial sorbents like Carbotrap 100® and Tenax TA® proved to be unselective both in the uptake and in the release steps. The molecular origins of the observed selectivity were traced by theoretical calculations in the presence of multiple electrostatic and CH–π interactions, possible only in the case of QxCav–aromatic analyte complexes.

Introduction

The widespread need for fast, reliable, highly sensitive and selective analytical methodologies for measuring volatile organic compounds (VOCs) in the environment poses a fascinating challenge to the chemical community.

Most VOCs are an important class of water and atmospheric pollutants and a number of them are recognized as substances with a high research priority by international organizations.[1] In particular, the detection of airborne aromatic hydrocarbons (BTX) constitutes a long standing problem, due to the need to measure with high precision extremely low benzene concentrations in the presence of overwhelming amounts of other aliphatic and aromatic hydrocarbons. Most of the approaches implemented so far to solve the problem rely either on spectroscopic methods (LIDAR, *etc.*)[2] or on gas chromatography/mass spectrometry (GC/MS).[3] This second approach requires the preconcentration of the analytes in traps before chromatographic separation and determination. For the determination of BTX in ambient air, BTX are first preconcentrated mostly using the sorbent sampling technique or the cryogenic sampling method.[3,4] For the analysis of BTX in water, various methods are used for preconcentration, but the dynamic headspace and purge-and-trap (PT) techniques are the most preferred, especially for the determination of purgeable priority pollutants listed by the US Environmental Protection Agency.[5]

Ideally a sorbent material used for preconcentrating BTX should have the following features, *i.e.* large breakthrough volumes for the enrichment of the compounds, complete desorption of the analytes at moderate temperatures, good thermal stability and high selectivity for the enrichment of organic compounds in comparison with the matrix so that no retention of water vapor can occur. However, the materials used as sorbents (activated carbon, Tenax TA®, graphitized carbon blacks such as Carbotrap 100® and Carbotrap 300®, *etc.*) have a common limitation, since they are unselective both in the adsorption and in the desorption processes.

The use of molecular receptors to enhance selectivity has been widely exploited in analytical separative methodologies ranging from capillary GC to liquid chromatography (HPLC).[6,7] In contrast, this approach has been scarcely applied in extraction techniques, such as purge-and-trap or headspace sampling techniques.[8]

This paper presents an innovative dynamic headspace-based approach to sampling of BTX using cavitands, highly versatile molecular receptors,[9] grafted on silica gel. The cavitands shown in Fig. 1 were chosen as molecular receptors for this study since their molecular recognition properties have been extensively studied in the solid state,[10] in solution[10b,c,e] and

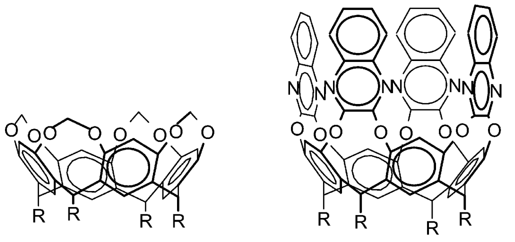
MeCav **QxCav**

Fig. 1 Chemical structures of methylene (MeCav) and quinoxaline (QxCav) bridged cavitands.

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† Electronic supplementary information (ESI) available: synthetic procedures for the preparation of cavitands **2**, **3**; ^{29}Si and ^{13}C CP/MAS NMR spectra of MeCav and QxCav coated silica; desorption pattern of BTX observed for Tenax TA® at 50 °C; GC traces obtained from the desorption at 75 °C of the BTX mixture trapped on AXCav trap and Carbotrap 100®. See http://www.rsc.org/suppdata/nj/b2/b210942e/

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in the gas phase.[11] Particularly important for the design of selective sorbents is the understanding of host–guest interactions at the solid–gas interface, which can be partially inferred from gas-phase and solid-state studies.

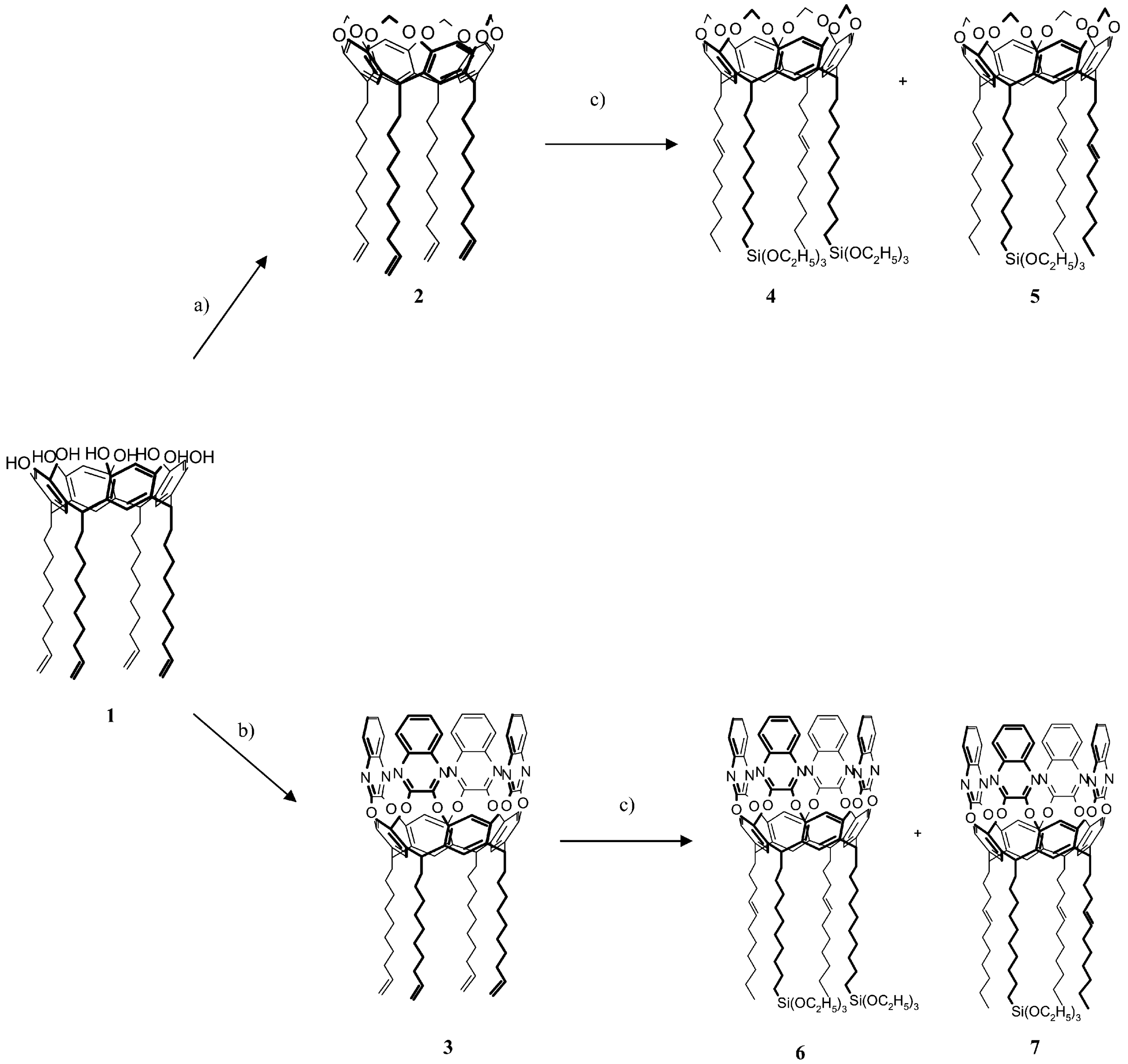
The present work will cover the following issues: (i) preparation of silyl-footed cavitands, selection of the grafting procedures and characterization of the resulting materials, (ii) testing of the performances of the trapping materials towards BTX and comparison with the performances of commonly used sorbents, (iii) theoretical investigation of the molecular origins of selectivity in complexation.

Results and discussion

Preparation of the cavitand receptors

For this work we have chosen two different cavitand receptors having respectively methylene (MeCav) and quinoxaline (QxCav) bridges, delimiting cavities of respectively 3.3 Å,[10a] and 8.3 Å[10c] depth (Fig. 1). The nature of bridging groups in cavitands controls the shape and dimensions of the cavities, as well as selectivity in complexation *via* a combination of shape complementarity and CH–π interactions.[12] MeCav has a shallow cavity capable only of CH–π interactions between the resorcinarene π-basic cavity and suitable guests having acidic methyl groups like CH_3CN and CH_3NO_2.[10b] QxCav has a much deeper cavity which completely engulfs aromatic guests, providing additional weak CH–π interactions with the cavity walls. In particular the complexation properties of QxCav toward aromatic compounds have been demonstrated both in solution[10e] and in the gas phase.[11]

To be used as traps for dynamic headspace–gas chromatography or purge-and-trap–gas chromatography analysis, cavitands have to be grafted on a solid support,[13] in our case silica gel. This requires the introduction of suitable substituents at the lower rim. Among the grafting reagents known, triethoxysilane was chosen because of the mild grafting conditions and the possibility to introduce it regioselectively on double bonds, *via* hydrosilylation procedures. The building block for this purpose is resorcinarene **1**,[12] having four terminal double bond chains at the lower rim. The synthetic protocol employed for cavitands **2** and **3** (Scheme 1) requires two steps: functionalization at the upper rim with the appropriate bridging group, followed by hydrosilylation at the lower rim.



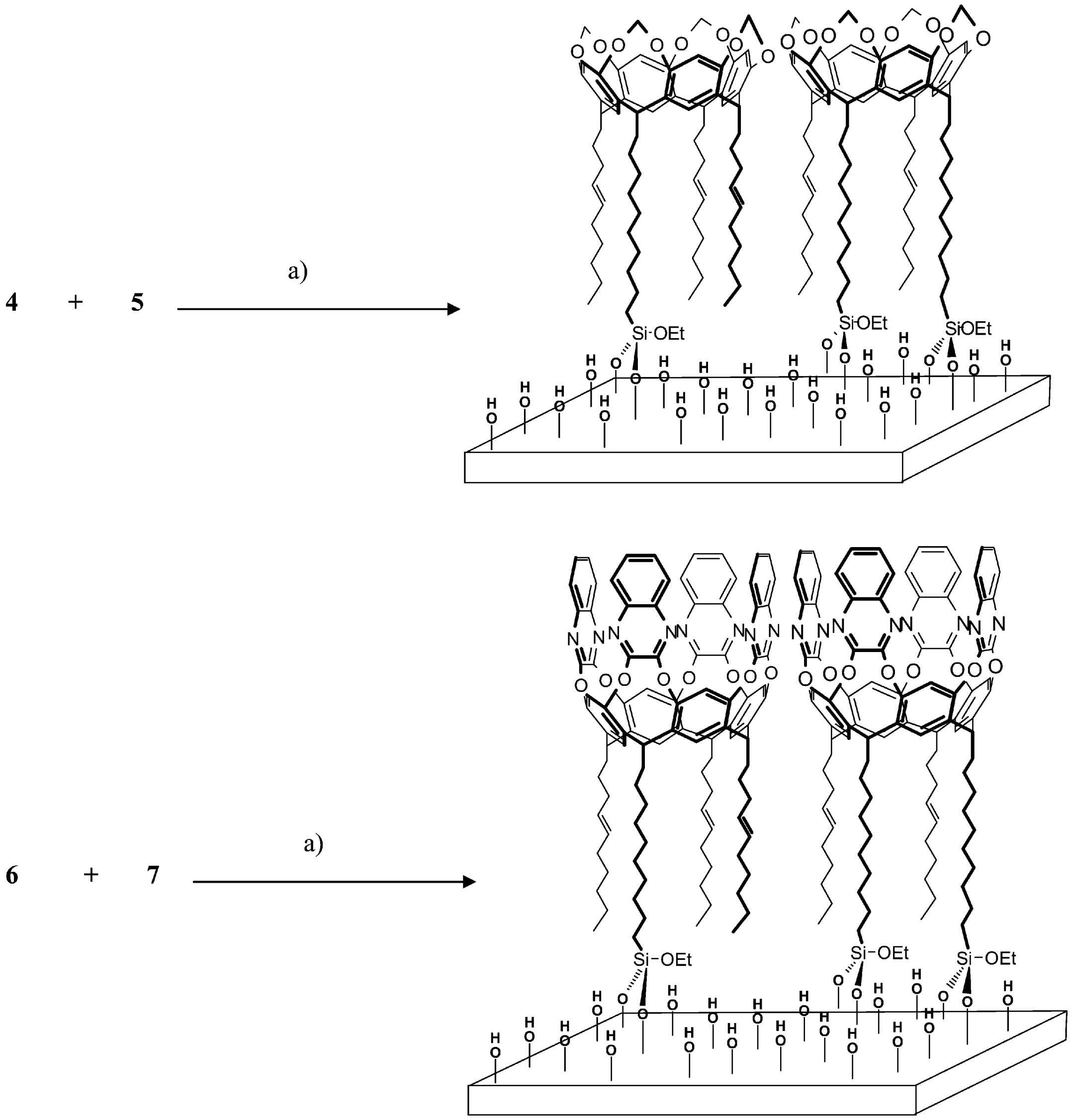
Scheme 1 Synthesis of cavitands **2**–**7**: a) dibromochloromethane, K_2CO_3, dry DMA, 40–50 °C, 16 h; b) 2,3-dichloroquinoxaline, K_2CO_3, dry DMA, 40–50 °C, 16 h; c) triethoxysilane, $RhCl(PPh)_3$, dry toluene, 70 °C, 36 h. The positions of internal double bonds are arbitrary. In the derivatives **4** and **6** the triethoxysilyl groups can be vicinal or distal.

The fourfold bridging reactions were made following published procedures using respectively bromochloromethane,[14] and 2,3-dichloroquinoxaline.[10d] The hydrosilylation reaction was tested using two different catalysts: (H_2PtCl_6)[15] and $[RhCl(PPh_3)_3]$.[16] The first one led exclusively to double bond isomerization to internal olefins, while Wilkinson's catalyst favored the formation of mono- and di-silylated derivatives **4/5** and **6/7** (Scheme 1), along with isomerization of the remaining double bonds. Both **5/7** mono- and **4/6** di-ethoxysilyl derivatives were isolated and characterized separately.

Grafting of the cavitands onto silica gel

The silica gel was activated by placing it in refluxing 18% HCl. The activation of the silica gel caused a progressive reduction of the particle dimensions. Under these conditions only the 35–70 mesh silica gel cartridges allow an optimal nitrogen flow for subsequent BTX analyses. The optimal 10% (w/w) grafting of the two cavitands was obtained by reacting the triethoxysilyl derivatives with activated silica in CH_2Cl_2 at room temperature in a 3:10 (w/w) ratio (Scheme 2). Toluene, the typical solvent used in these grafting procedures, was replaced by CH_2Cl_2 since it led to undesired contamination of the resulting cartridge. Under these milder conditions the effective cavitand–silica gel w/w ratio obtained was about one third of the theoretical value (Table 1). The remaining unreacted silylated cavitands were recovered from the organic solution.

Elemental analyses and ^{29}Si and ^{13}C solid state NMR were used to characterize the silica immobilized receptors. The elemental analyses are reported in Table 1. The ^{29}Si-NMR spectra in cross-polarization conditions of the two silica-bonded cavitands have been recorded (see ESI†). Both spectra exhibit a large signal belonging to the silica support. The overall signal is constituted by three partially superimposed peaks: Q^2, in the range −92.1/−91.5 ppm, assigned to silicon atoms bonded to two hydroxyl groups, Q^3, in the range −101.7/−101.3 ppm, assigned to silicon atoms with one hydroxyl group, and Q^4, in the range −111.8/−111.4 ppm, assigned to silicon atoms without hydroxyl groups, placed in the bulk of the silica structure. The intensity ratio of these three components, Q^2, Q^3, Q^4, does not reflect the real concentration of the corresponding species in the sample, because in the cross-polarization pulse sequence the intensity of each signal is enhanced in a measure proportional to the number and the proximity of surrounding protons. Beside this signal, in the region between −70 and −55 ppm, two other signals of low intensity appear (T^2 and T^3), belonging to silicon atoms bonded to the organic phase. The low intensity of these peaks is due to the scarce sensitivity of ^{29}Si solid state NMR, that could not be enhanced either with longer accumulation times or with larger quantities of sample (the rotors were completely filled up). The presence of grafted



Scheme 2 Immobilization of cavitands **4**, **5**, **6**, **7**: a) actived silica gel, dry CH_2Cl_2, RT, 2 days.

Table 1 Elemental analyses for MeCav and QxCav grafted materials

Immobilized cavitand	Element	Theoretical values[a] (%)	Experimental values (%)	Effective cavitand–silica gel ratio (%)
MeCav	C	17.62	6.95	11.8
QxCav	C	17.45	6.63	11.4
	N	1.60	0.42	7.9

[a] Calculated for a 3:10 w/w ratio.

cavitands has been independently confirmed *via* ^{13}C solid state NMR analyses performed on the same samples. The ^{13}C NMR spectra (see ESI†) clearly show the presence of an organic phase, exhibiting aromatic and aliphatic carbons belonging to the cavitand structures.

The thermal stability of the immobilized cavitands was determined *via* thermogravimetric analyses in order to avoid decomposition during their use as sorbent materials. Both MeCav and QxCav start to decompose at $T > 280\,°C$, well above the cartridge operating conditions.

Analytical evaluation of the cavitand sorbents

The two cavitand sorbents were tested for the selective trapping of environmentally relevant BTX (benzene, toluene, xylenes) to verify if their molecular recognition properties were retained at the gas–solid interface. All tests were carried out in parallel with Tenax TA® and Carbotrap 100®, two commonly used sorbents for VOCs. Before testing, determination of the sampling capacity of the sorbents was performed by calculating the breakthrough volumes of the cartridges.

Breakthrough volumes

Breakthrough volumes were calculated connecting two tubes in tandem configuration and trapping the volatile analytes by varying the volume of the sampling gas until a sampling volume of 3.6 L was achieved (see Experimental section). Breakthrough is defined as the volume occurring when in the second tube the signal of the analyte exceeds 5% with respect to the total recovered. Sorbents are usually selected on the basis of a sampling capacity of at least 1 L per sorbent tube.[17]

Our experiments showed that traps containing 10% of QxCav immobilized on silica gel were characterized by a sampling capacity greater than 3.6 L with respect to BTX. Data obtained by using traps containing only 3% of immobilized cavitand showed scarce reproducibility and irregularly shaped chromatographic peaks. This behavior could be ascribed to the interactions of the analytes with silica gel as a consequence of the presence of a reduced organic layer. The breakthrough volumes of traps containing MeCav could not be evaluated, since they do not complex BTX.

Selective trapping of BTX

The following BTX analyte composition was chosen for the testing procedure: benzene (55 μg L^{-1}), toluene (160 μg L^{-1}), *m*-xylene (160 μg L^{-1}), *p*-xylene (160 μg L^{-1}) and *o*-xylene (550 μg L^{-1}) in pentane. These values reproduce the typical composition ratio of aromatic compounds in indoor polluted conditions. The analytes, flushed with nitrogen, were adsorbed by the traps under dynamic headspace conditions and subsequently thermally desorbed and cryofocused into a GC-MS instrument for a semi-quantitative determination (see Experimental section). Sequential desorption trials were performed by heating the sorbent tubes from 50 °C to 150 °C with 25 °C steps.

Desorption experiments at 50 °C allowed cavitand traps to release uncomplexed analytes. The MeCav trap retained an extremely limited amount of BTX, which were totally desorbed already at 50 °C. This result is in accordance with both solution and gas-phase experiments, indicating the inability of this type of cavity to complex aromatic guests.[18] By contrast, the QxCav trap released pentane already at 50 °C as uncomplexed aliphatic hydrocarbon, whereas the aromatic compounds were desorbed at higher temperatures.

In order to verify that aliphatic hydrocarbons were not complexed by QxCav, in a control experiment run under the same conditions these traps were exposed to a mixture of pentane, octane and cyclohexane (50 μg L^{-1} each in hexane): no signal was observed at any desorption temperature, indicating the inability of the cavitand to complex this class of compounds.

The BTX desorption patterns observed for QxCav sorbents at 75 °C, 100 °C and 150 °C are reported in Fig. 2 and compared with those of Carbotrap 100® under the same conditions (Tenax TA® desorbed completely benzene already at 50 °C, see ESI†). The histograms clearly evidence a trend toward the selective release of benzene moving from the aspecific Carbotrap 100® trap to the QxCav sorbent. In the case of QxCav, benzene was found to be selectively desorbed, even though it was present at lower concentration in the mixture. In the subsequent desorption steps at 100 °C and 150 °C, toluene and xylenes were respectively the major analytes desorbed from all traps. Desorption experiments carried out on the same aromatic composition without toluene validated the performance of QxCav in the selective release of benzene (Fig. 3), confirming toluene as the only major interferent. The corresponding chromatographic traces obtained from desorption experiments at 75 °C for QxCav and Carbotrap 100® traps are reported in the ESI.† Considering that both Tenax TA® and Carbotrap 100® are entirely composed by sorbent material, whereas in QxCav traps only 10% of receptors are loaded on the silica surface, the efficiency of cavitand traps is remarkably high.

Molecular origin of selectivity

The data reported clearly point out the importance of the depth of the cavity in the complexation of BTX by cavitand receptors. In fact, the quinoxaline walls of the cavity offer weak multiple electrostatic and CH–π interactions to complementary guests, such as aromatic hydrocarbons. A theoretical investigation was therefore undertaken for a better understanding of the observed selectivity on a molecular basis.

The complexing abilities of MeCav and QxCav towards benzene and toluene were theoretically investigated by semiempirical molecular orbital calculations using the PM3 model[19] leading to the optimized geometries of the benzene and toluene complexes shown in Figs. 4 and 5.

The optimized geometries of the QxCav ⊃ benzene and QxCav ⊃ toluene complexes are in agreement with the molecular geometry of the QxCav ⊃ fluorobenzene complex obtained by crystal structure analysis.[10e] The complexes are stabilized by weak attractive host–guest interactions (red dots in Figs. 4 and 5) involving π electrons of the host, with two C–H$_{\text{guest}}$ bonds aligned along the direction of the π orbital of the interacting C$_{\text{host benzene}}$ atoms. By contrast, in the case of MeCav complexes the guest is just perching on top of the cavity, with host–guest contacts at the limit of the sum of the van der Waals radii.

The complexation energies ΔE, calculated as $\Delta E = E_{\text{complex}} - [E_{\text{host}} + E_{\text{guest}}]$, where E_{complex} is the energy of the complex and E_{host} and E_{guest} are the energies of the host and of the guest in the geometry observed in the complex, are summarized in Table 2. This calculation gives the interaction energy between the host and the guest in the complex and accounts for the energy necessary to extract the guest from the frozen host. This approach seems reasonable in view of

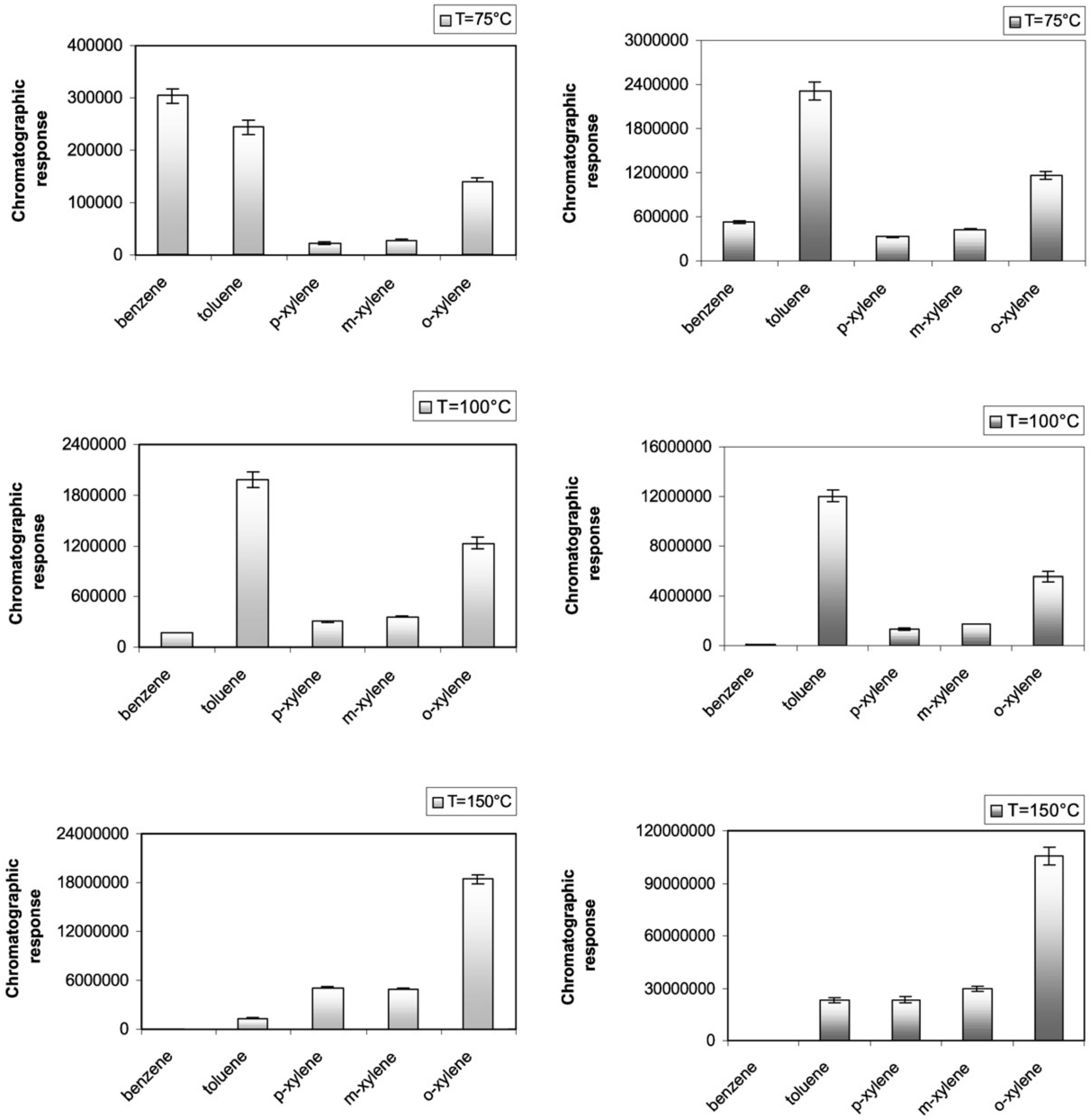


Fig. 2 Comparison of the desorption patterns of QxCav (left) and Carbotrap 100® (right) sorbents at 75 °C, 100 °C and 150 °C.

the comparison with the experimental data of the selectivity measured with the host molecule immobilized on a solid matrix, where the release is mimicked. In the case of the toluene guest molecule, two possible orientations of the toluene inside the host cavity were selected as starting points for the geometry optimizations: a) toluene-in when the CH_3 fits into the cavity, b) toluene-out when the CH_3 sticks out of the cavity. The calculations predict that QxCav is a better receptor than MeCav for aromatic guests. In addition, the

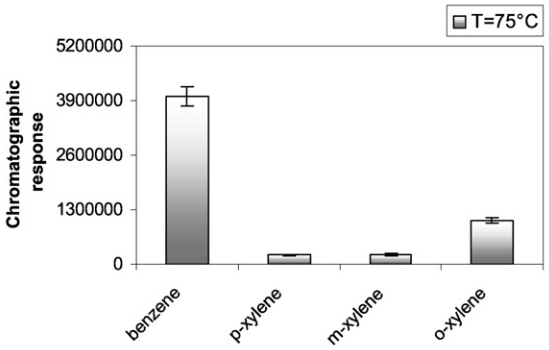


Fig. 3 Desorption pattern observed for the QxCav trap at 75 °C towards benzene and xylenes (the analyte composition is that of Fig. 2 without toluene).

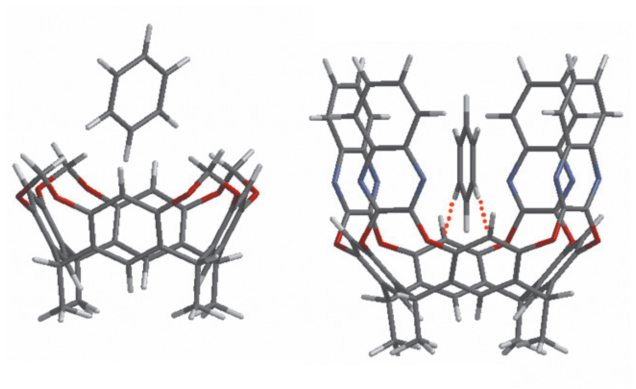


Fig. 4 Geometry-optimized structure of MeCav–benzene and QxCav–benzene complexes. In both cavitands the aliphatic chains have been replaced with methyl groups.

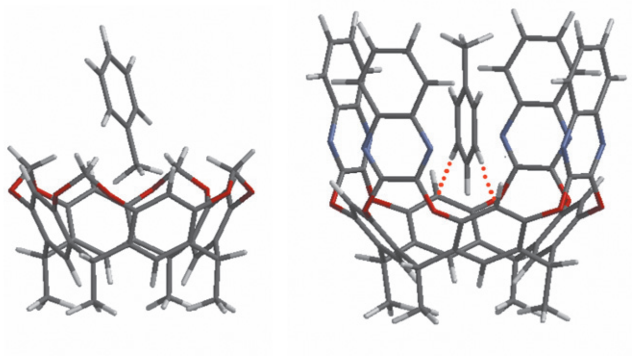


Fig. 5 Geometry-optimized structure of MeCav–toluene and QxCav–toluene complexes. In both cavitands the aliphatic chains have been replaced with methyl groups.

complexation energies of benzene and toluene-out complexes of QxCav have almost the same value and are both preferred over toluene-in. Experimentally, a slight preference for toluene *versus* benzene is shown by QxCav both in solution[10e] and in the gas phase.[11b]

The analysis of the Molecular Electrostatic Potential plotted onto the molecular surface of the complexes explains this selectivity. In fact, for benzene and toluene-out, the negative electrostatic potential area on the benzene nucleus is just faced on the complementary positive electrostatic potential area on the quinoxaline nucleus owing to the presence of the quinoxaline rings, whereas when the toluene points the methyl group inside the cavity the complementarity between the electrostatic potential of host and guest is partially destroyed making the interaction less attractive (Fig. 6).

Conclusions

In this work we have synthesized, characterized and tested a new sorbent material for the selective detection of BTX. The molecular recognition properties of QxCav as a receptor were exploited at the solid–gas interface by grafting cavitands silylated at the lower rim onto silica gel. The resulting sorbent material conveys its complexation properties at two levels: (i) in the adsorption phase, where it selectively retains BTX at the ppb level in the presence of aliphatic hydrocarbons; (ii) in the release phase, where the typical desorption scheme of commercial sorbents like Carbotrap 100® is altered in favour of benzene. The ineffectiveness of the small MeCav receptor suggests that the presence of an extended and deep cavity is pivotal for BTX complexation.

The molecular origin of the observed selectivity was investigated by theoretical calculations, which indicated in the presence of multiple electrostatic and CH–π interactions the driving force for the complexation of aromatic guests. The results of the theoretical calculations are consistent both with the experimental GC-MS data reported here and with the previous solid state, solution and gas phase studies.

The QxCav sorbent material represents the first step toward a new generation of selective sorbents specifically designed for on-line monitoring of benzene at trace level. The possibility to adsorb BTX from air and release benzene in pure form on highly sensitive metal oxide semiconductor sensors, overcoming their selectivity limitations, will open the way for real-time onsite benzene monitoring.[20] To reach this target, new cavitands with enhanced toluene *versus* benzene affinity are required. Currently we are pursuing this goal.

Table 2 Complexation energies (kJ mol^{-1}), $\Delta E = E_{\text{complex}} - [E_{\text{host}} + E_{\text{guest}}]$ for the MeCav and QxCav host molecules and the guests benzene and toluene

Host	Benzene	Toluene-in	Toluene-out
MeCav	−1.0	−1.2	−1.3
QxCav	−6.85	−1.30	−6.88

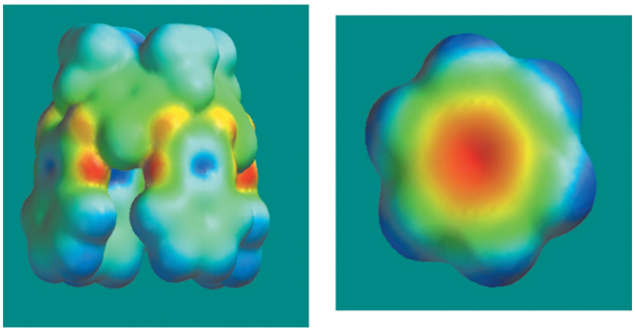


Fig. 6 Molecular electrostatic potential (MEP) plotted onto the molecular surfaces of QxCav and benzene. Color codes: red = negative values; blue = positive values).

Experimental

General

Melting points (m.p.) were obtained on a Büchi melting-point apparatus and were uncorrected; ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC300 (Bruker, Karlsruhe, Germany) spectrometer at 300 K; chemical shifts were given in ppm ($\delta_{\text{TMS}} = 0$) using the residual resonances of the deuterated solvent ($\delta = 7.25$ for chloroform and $\delta = 2.49$ for DMSO) as internal reference. FT-IR spectra were recorded on a NICOLET 5PC FT-IR spectrometer (Thermo Electron Corporation, Waltham, MA, USA). TLC was performed on aluminium sheets precoated with silica gel 60 F$_{254}$ (Merck, Darmstadt, Germany); column chromatography was performed on silica gel 70–230 mesh ASTM (Merck). Mass spectra were obtained with a single-stage quadrupole mass spectrometer (Finnigan MAT SSQ 710) (Thermo Finnigan MAT, Bremen, Germany) under chemical ionization (CI) conditions. ^{29}Si and ^{13}C solid state NMR spectra were acquired on a Bruker MSL 200 spectrometer using 4 mm zirconia rotors and a spinning rate of 5200 Hz. For ^{29}Si NMR spectra the standard cross-polarization pulse sequence was adopted with the following parameters: pulse length for 5 µs (90°), contact time of 5 ms, 120 000 scans for each spectrum, repetition rate of 2 s and frequency sweep of 20 000 Hz. ^{13}C NMR spectra were acquired always in cross-polarisation conditions with the following parameters: pulse length of 4 µs (90°), contact time of 5 ms, 80 000 scans for each spectrum, repetition rate of 2 s and frequency sweep of 20 000 Hz. ^{29}Si chemical shifts are referred to TMS at 0.00 ppm and ^{13}C chemical shifts are referred to the carbonyl of glycine at 176.03 ppm. Thermogravimetric analyses were performed using a Perkin-Elmer TGA7 (Perkin-Elmer, Cupertino, CA, USA). Elemental analyses were carried out on a CHNS-O EA 1108 Elemental Analyzer (Carlo Erba, Milan, Italy). All commercially available chemicals were used without further purification unless otherwise specified. All anhydrous solvents used were dried over 3 and 4 Å molecular sieves.

Synthesis of silylated cavitands

Resorcinarene **1** was prepared following the literature procedure.[21] The syntheses of cavitands **2** and **3** are reported in the ESI.†

Cavitands 4 and 5. Triethoxysilane (0.67 mL, 3.63 mmol) and $\mathrm{RhCl(PPh_3)_3}$ (7.0 mg, 7.6×10^{-3} mmol) as catalyst (ratio $\mathrm{R_3SiH/Rh} = 480$) were added, under argon, to a solution of cavitand **2** (0.66 g, 0.60 mmol) in dry toluene (40 mL). The colourless solution was stirred at 70 °C for about 24 hours. Further triethoxysilane (0.3 mL, 1.62 mmol) and $\mathrm{RhCl(PPh_3)_3}$ (7.0 mg, 7.6×10^{-3} mmol) were added and the solution was heated at 70 °C for a further 16 hours. After cooling to room temperature the solvent was removed, under vacuum; the residue was purified by column chromatography ($\mathrm{SiO_2}$, $\mathrm{CH_2Cl_2}$) to give the cavitand **4** in 21% yield (0.18 g) and cavitand **5** in 62% yield (0.47 g), both as oil. **4**: $R_f = 0.42$; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.10$ (s, 4H; ArH), 6.47 (s, 4H; ArH), 5.72 (d, $J = 7.2$ Hz; 4H; C$H_{2\mathrm{out}}$), 5.40 (m, 4H, RCH = CHR), 4.72 (t, $J = 8.0$ Hz, 4H; RCHAr$_2$), 4.41 (d, $J = 7.2$ Hz, 4H; C$H_{2\mathrm{in}}$), 3.83 (q, 12H; SiOCH_2CH$_3$), 2.18 (m, 8H; RCH_2CHAr$_2$), 2.07 (m, 8H; CH_2CH=CHCH_2), 1.23 (m, 52H; CH_2), 1.20 (t, 18H SiOCH$_2$CH_3), 0.90 (bt, 6H, RCH_3), 0.62 (bt, 4H, SiCH_2); MS (CI): m/z (%): 1419 (100) $[\mathrm{MH}]^+$. **5**: $R_f = 0.56$; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.10$ (s, 4H; ArH), 6.47 (s, 4H; ArH), 5.73 (d, $J = 7.2$ Hz, 4H; C$H_{2\mathrm{out}}$), 5.39 (m, 6H; RCH=CHR), 4.72 (t, $J = 8.0$ Hz, 4H; RCHAr$_2$), 4.41 (d, $J = 7.2$ Hz, 4H; C$H_{2\mathrm{in}}$), 3.83 (q, 6H; SiOCH_2CH$_3$), 2.18 (m, 8H; RCH_2CHAr$_2$), 2.07 (m, 12H; CH_2CH=CH$_2$), 1.23 (m, 46H; CH_2), 1.19 (t, 9H SiOCH$_2$CH_3), 0.89 (bt, 9H, RCH_3), 0.62 (bt, 2H, SiCH_2); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 154.8$ (C, resorcinarene), 138.4 (C, resorcinarene), 132.0–123.7 (C=C), 120.6 (C, resorcinarene), 116.4 (C, resorcinarene), 99.5 (OCH_2O), 77.0 (SiOCH_2CH$_3$), 36.3 (CHAr$_2$), 32.6–22.7 (CH_2, chain), 17.9 (SiOCH$_2$$CH_3$), 14.0 ($CH_3$, terminals); MS (CI): m/z (%): 1255 (100) $[\mathrm{MH}]^+$.

Cavitands 6 and 7. Triethoxysilane (0.71 mL, 3.85 mmol) and $\mathrm{RhCl(PPh_3)_3}$ (7.7 mg, 8.3×10^{-3} mmol) as catalyst (ratio $\mathrm{R_3SiH/Rh} = 460$) were added, under argon, to a solution of cavitand **4** (0.99 g, 0.64 mmol) in dry toluene (70 mL). The colourless solution was stirred at 70 °C for about 24 hours. Further triethoxysilane (0.35 mL, 1.90 mmol) and $\mathrm{RhCl(PPh_3)_3}$ (7.7 mg, 8.3×10^{-3} mmol) were added and the solution was heated at 70 °C for a further 16 hours. After cooling to room temperature, the solvent was removed under vacuum and the residue purified by column chromatography ($\mathrm{SiO_2}$, $\mathrm{CH_2Cl_2}$) to give cavitand **6** in 7% yield (0.074 g) and cavitand **7** in 45% yield (0.49 g), both as pale yellow powder. **6**: $R_f = 0.44$; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 8.17$ (s, 4H; ArH), 7.78 (m, 8H; ArH, part AA′ of a AA′BB′ system), 7.47 (m, 8H; ArH, part BB′ of a AA′BB′ system), 7.22 (s, 4H; ArH), 5.60 (t, $J = 8.0$ Hz, 4H; RCHAr$_2$), 5.43 (m, 4H; RCH=CHR), 3.83 (q, 12H; SiOCH_2CH$_3$), 2.23 (m, 8H, RCH_2CHAr$_2$), 2.00 (m, 8H; CH_2CH=CHCH_2), 1.32 (m, 52H; CH_2), 1.22 (t, 18H SiOCH$_2$CH_3), 0.90 (bt, 6H, RCH_3), 0.62 (bt, 4H, SiCH_2); MS (CI): m/z (%): 1873 (100) $[\mathrm{MH}]^+$. **7**: $R_f = 0.61$; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 8.17$ (s, 4H; ArH), 7.78 (m, 8H; ArH, part AA′ of a AA′BB′system), 7.47 (m, 8H; ArH, part BB′ of a AA′BB′ system), 7.22 (s, 4H; ArH), 5.60 (t, $J = 8.0$ Hz, 4H; RCHAr$_2$), 5.43 (m, 6H; RCH=CHR), 3.83 (q, 6H; SiOCH_2CH$_3$), 2.23 (m, 8H, RCH_2CHAr$_2$), 2.03 (m, 12H; CH_2CH=CHCH_2), 1.32 (m, 46H; CH_2), 1.19 (t, 9H SiOCH$_2$CH_3), 0.88 (bt, 9H, RCH_3), 0.62 (bt, 2H, SiCH_2); ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 152.5$ (C, resorcinarene), 152.4 (C, resorcinarene), 139.6 (C, quinoxaline), 135.7 (C, quinoxaline), 132.0–130.7 (C=C), 128.9 (C, quinoxaline), 127.7 (C, quinoxaline), 124.6 (C=C), 123.7 (C=C), 123.3 (C, resorcinarene), 118.7 (C, resorcinarene), 34.2 (SiOCH_2), 32.6–22.7 (C, chain), 17.9 (SiOCH$_2$$CH_3$), 14.1 ($CH_3$, terminals); MS (CI): m/z (%): 1710 (100) $[\mathrm{MH}]^+$.

Preparation of supported silica gel

Activation of silica gel (35–70 mesh ASTM). A suspension of silica gel (6.5 g, 35–70 mesh ASTM) in $\mathrm{HCl/H_2O}$ (100 mL, 1:1) was stirred at the reflux temperature for 9 hours. The silica gel was filtered and washed with $\mathrm{H_2O}$ until pH 4, then dried by heating to 110 °C under vacuum for one day.

Grafting of cavitands 4 and 5. Activated silica gel (6.50 g) was added to a solution of **4** and **5** (1.95 g, approximate ratio **4/5** = 1/3) in dry $\mathrm{CH_2Cl_2}$ (100 mL), using a ratio cavitand/activated silica gel = 30% (w/w). The suspension was stirred at room temperature for two days. The residue was filtered and washed with $\mathrm{CH_2Cl_2}$ to give 7.14 g of supported silica gel. ^{29}Si CP/MAS NMR: $\delta = -111.8/-111.4$ (Q^4, 20.7%), $-101.7/-101.3$ (Q^3, 66.9%), $-92.1/-91.5$ (Q^2, 10.9%), -69.4 (T^3, 0.7%), -62.1 (T^2, 0.7%); ^{13}C CP/MAS NMR: $\delta = 154.8$ (C, resorcinarene), 137.7 (C, resorcinarene), 132.1 (C=C), 119.7 (C, resorcinarene), 117.1 (C, resorcinarene), 100.6 (OCH$_2$O), 48.1 (SiOCH$_2$CH$_3$), 28.6–22.2 (C, chain), 15.6 (SiOCH$_2$$CH_3$), 11.8 ($CH_3$, terminal); thermogravimetric analysis (40–600 °C, 10 °C min^{-1}): decomposition temperature > 280 °C; elemental analysis calcd. (%) for $\mathrm{C_{74}H_{102}O_9Si}$ (calculated for a 3:10 w/w ratio monosilylated cavitand/silica): C 17.62, H 2.04; found: C 6.95, H 1.01%.

Grafting of cavitands 6 and 7. Activated silica gel (4.90 g) was added to a solution of **6** and **7** (1.47 g, approximate ratio **6/7** = 1/7) in dry $\mathrm{CH_2Cl_2}$ (60 mL), using a cavitand/activated silica gel ratio equal to 30% (w/w). The suspension was stirred at room temperature for two days. The residue was filtered and washed with $\mathrm{CH_2Cl_2}$ to give 5.31 g of supported silica gel. ^{29}Si CP/MAS NMR: $\delta = -111.8/-111.4$ (Q^4, 25.2%), $-101.7/-101.3$ (Q^3, 60.0%), $-92.1/-91.5$ (Q^2, 10.1%), -67.1 (T^3, 1.3%), -56.5 (T^2, 3.3%); ^{13}C NMR: $\delta = 152.3$ (C, resorcinarene), 137.5 (C, chain), 130.0–128.0 (C, resorcinarene + C, chain + C=C, chain), 48.3 (SiOCH$_2$CH$_3$), 29.1 (C, chain), 15.4 (SiOCH$_2$$CH_3$), 12.7 ($CH_3$, terminal); thermogravimetric analysis (40–600 °C, 10 °C min^{-1}): decomposition temperature > 280 °C; elemental analysis calcd. (%) for $\mathrm{C_{102}H_{110}N_8O_9Si}$ (calculated for a 3:10 w/w monosilylated cavitand/silica ratio): C 17.45, H 1.58, N 1.60; found: C 6.63, H 0.79, N 0.42.

Adsorbent tube preparation. The adsorbent cartridges were prepared by packing glass tubes (160 mm × 4 mm ID × 6 mm OD) with 200 mg of trapping materials (cavitands immobilised on silica gel) under atmospheric pressure; silanized glass wool plugs were utilised to retain the adsorbent within the tubes. The cartridges were conditioned by heating to 250 °C for 8 h under a flow of ultrahigh-purity nitrogen. After conditioning each cartridge was immediately capped with Swagelok to prevent diffusive sampling of ambient air moisture and other constituents. Adsorption tubes filled with Tenax TA® (110 mg, 20–35 mesh, Chrompack, Middelburg, The Netherlands) and Carbotrap 100® (400 mg, 20–40 mesh, Supelco Park, Bellefonte, PA, USA) were used as reference trapping materials.

Reagents and solutions. All chemicals used were of highest available purity and were obtained from different sources. A stock standard solution (1000 mg L^{-1}), *i.e.* a mixture of BTX in n-pentane, was prepared from pure compounds in calibrated flasks. Further dilutions of this stock standard solution were made to prepare the different working standard solutions required in the experiments. All the solutions were kept refrigerated at 4 °C.

Breakthrough volumes. Two sorbent tubes in tandem configuration were analysed: an aliquot of gas containing about 6 µg of each compound was injected into the first tube under a flow of pure nitrogen at 60 mL min^{-1}. After periods ranging from

20 to 60 min the flow was discontinued and the two tubes separated and analysed.

Sampling procedure. The analytes were concentrated from an aqueous solution (40 mL) using a dynamic headspace technique with adsorption on the selected materials. Benzene (55 μg L^{-1}), toluene, *m*-, *p*-xylene (160 μg L^{-1} per component) and *o*-xylene (550 μg L^{-1}) were placed in a closed flask at 45 °C and nitrogen was passed through the flask at a rate of 40 mL min^{-1} for 10 min. The volatile substances stripped by nitrogen were adsorbed by the trap that was subsequently backflushed with a stream of nitrogen for 5 minutes to eliminate any residual water that might have been adsorbed. All the analyses were replicated three times.

GC-MS analyses. Sequential desorption experiments were performed on a TD 800 (Fisons Instruments, Milan, Italy) thermal desorption system on-line coupled to a GC 8000 gas chromatograph interfaced to a MD 800 quadrupole mass spectrometer with a Mass Lab data system (Fisons Instruments). A deactivated fused-silica column (Fisons Instruments) was used as a transfer line between the cold trap and the analytical column DB-WAX (30 m × 0.25 mm, d_f 0.25 μm J. & W. Scientific, Folsom, CA, USA). The volatile compounds were thermally desorbed and injected into the gas chromatograph using a thermal desorption cold trap. Sequential desorption experiments were performed heating the sorbent tubes from 50 to 200 °C with 25 °C steps for 10 minutes under a helium flow (10 mL min^{-1}). The desorbed substances were cryofocused in a silica capillary cooled at −120 °C by liquid nitrogen and then injected into the GC column by quickly heating the cold trap to 250 °C. Chromatographic separation of the aromatic substances was performed as follows: the oven temperature was held at 30 °C for 4 min and then programmed from 30 °C to 60 °C at 3 °C min^{-1} and from 60 °C to 150 °C at 15 °C min^{-1}. All the compounds were analyzed with the mass spectrometer operating in the electron impact (EI) mode at 70 eV; chromatograms were recorded by monitoring the total ion current in the 40–300 amu range. Interface and ion source were maintained at 230 °C and 190 °C respectively.

Computational details. Geometrical optimizations were carried out by a semiempirical molecular orbital method using the PM3 model in the PC Spartan Pro program.[22] MEP calculations: for QxCav and benzene the Molecular Electrostatic Potential maps were plotted onto the molecular surfaces corresponding to the isosurface at 0.002 e au^{-3}. The ranges of the electrostatic potential are: QxCav −52.54 (red), +28.89 (blue) kcal mol^{-1}. Benzene −15.72 (red), +12.38 (blue) kcal mol^{-1} (Fig. 6).

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