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Triptycene-Roofed Quinoxaline Cavitands for the Supramolecular Detection of BTEX in Air

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Abstract: Two novel triptycene quinoxaline cavitands (**DiTriptyQxCav** and **MonoTriptyQxCav**) have been designed, synthesized, and applied in the supramolecular detection of benzene, toluene, ethylbenzene, and xylenes (BTEX) in air. The complexation properties of the two cavitands towards aromatics in the solid state are strengthened by the presence of the triptycene moieties at the upper rim of the tetraquinoxaline walls, promoting the confinement of the aromatic hydrocarbons within the cavity. The two cavitands were used as fiber coatings for solid-phase microextraction (SPME) BTEX monitoring in air. The best performances in terms of enrichment factors, selectivity, and LOD (limit of detection) values were obtained by using the **DiTriptyQxCav** coating. The corresponding SPME fiber was successfully tested under real urban monitoring conditions, outperforming the commercial divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS) fiber in BTEX adsorption.

Introduction

Monitoring air pollution in urban and industrial areas requires the design of new air quality control systems capable of monitoring dangerous pollutants at trace concentrations. The detection of airborne aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX) constitutes a longstanding problem, as a result of the fact that high-precision measurement at trace concentrations of these nonpolar molecules is generally interfered with by overwhelming amounts of aliphatic hydrocarbons.[1] Presently, real-time air monitoring is performed by bulky conventional laboratory equipment that incurs high operating costs and requires trained users.[2]

The selective aromatic hydrocarbon complexation properties of tetraquinoxaline cavitands (**QxCav**)[3] have been recently exploited in our group to fabricate low-cost systems with sub-ppb_v detection limits of toxic volatile organic compounds (VOCs) in the presence of other airborne pollutants.[4] The performance of this prototype is enabled by a pre-concentrator unit filled with **QxCav** molecules capable of selectively trapping aromatic vapors at the gas–solid interface.[5] Complex formation is driven by multiple π–π and CH–π interactions between the aromatic guest and the deep, hydrophobic cavitand cavity.[1,6]

Rational design of **QxCav** molecular structures offers the possibility to further improve both the sensitivity and the selectivity of the preconcentrator. As reported by Diederich and co-workers,[7] quinone-based cavitands functionalized with bulky trypticene units at the upper rim are able to completely sterically encapsulate various guests in their closed "vase" conformation, increasing association constants and reducing guest-exchange rates owing to steric congestion.[8] The vase conformation is only present in the reduced hydroquinone state as a result of stabilizing intramolecular hydrogen bonding. Upon exposure to air, the hydroquinones oxidize to quinones, promoting the switching process from the closed vase to the open "kite" conformation, which is favored in the absence of hydrogen bonds by steric repulsion between amide and quinone moieties.[9] The kite conformation is not suitable for guest encapsulation within the shallow cavity and therefore these materials, although interesting, have reduced performance in oxygenated atmosphere. For the detection of aromatic hydrocarbons in air, cavitands with the following features were targeted: 1) Ability to entrap the guest at room temperature in the vase conformation during sampling; 2) insensitivity to the major interferents: water and aliphatic hydrocarbons; 3) release of the entrapped aromatic guests by thermal desorption at elevated temperatures. To this end, we designed a new class of triptycene tetraquinoxaline "roofed cavitands", **MonoTriptyQxCav** and **DiTriptyQxCav** (Figure 1) with one and two triptycene units, respectively, at the upper rim, to

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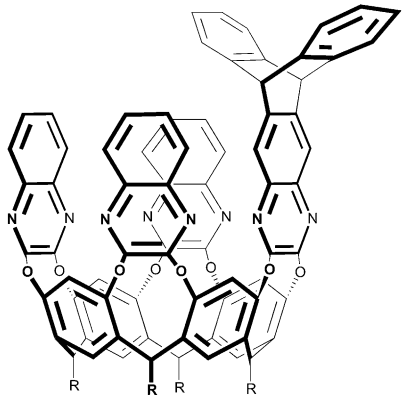
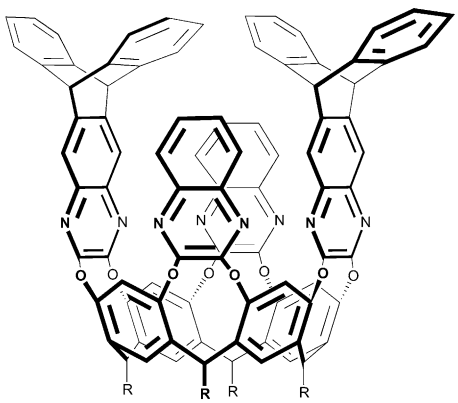


MonoTriptyQxCav



DiTriptyQxCav

Figure 1. Chemical structures of **MonoTriptyQxCav** and **DiTriptyQxCav**. R = C_6H_{13}.

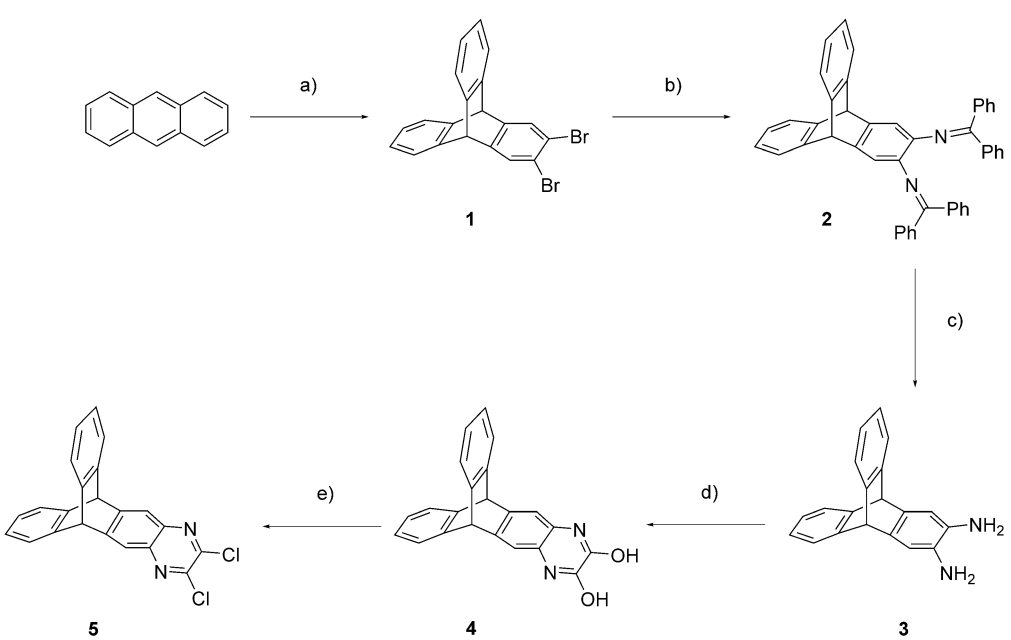
be used as solid-phase microextraction (SPME) coating for the selective detection of BTEX in air.

Results and Discussion

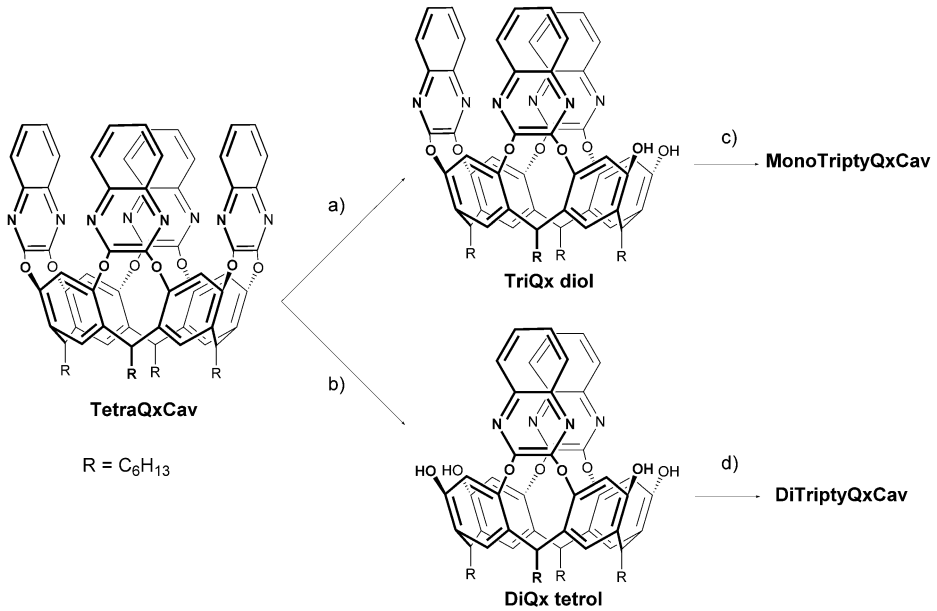
Cavitand synthesis

The two cavitands were prepared according to the following convergent synthetic approach: 1) synthesis of the triptycene-functionalized quinoxaline bridging unit **5** (Scheme 1); 2) synthesis of the partially bridged cavitand scaffolds; 3) introduction of one or two triptycene-functionalized bridging units (Scheme 2).

The multistep synthesis of **5** started with the Diels–Alder addition reaction of anthracene with benzyne, generated in situ from the reaction of *n*BuLi with 1,2,4,5-tetrabromobenzene to afford dibromotriptycene **1**.[10] The next step was the palladium-catalyzed Buchwald-Hartwig amination with benzophenone imine in refluxing toluene. This reaction allowed the insertion of two imines to obtain compound **2**. The amino protecting groups were then removed at room temperature with hydrochloric acid, followed by neutralization with sodium hydroxide to afford diaminotriptycene **3** after filtration. The alternative synthetic pathway reported in literature for the synthesis of derivative **3**,[11] a very useful building block for triptycene chemistry, proceeds through 5 synthetic steps and tedious purifications, to afford **3** in low overall yield. With this new protocol, inspired by a synthetic pathway developed for hexaaminotriptycene in 2012,[12] diaminotriptycene is synthesized in three steps with 50% process yield and only two chromatographic purifications. Due to the high reactivity of amino groups, compound **3** was used without any further purification for a con-



Scheme 1. Synthesis of **5**: a) 1,2,4,5-tetrabromobenzene, *n*BuLi, toluene, RT, 12 h, 62%; b) benzophenone imine, [$Pd_2(dba)_3$], *rac*-BINAP, NaO*t*Bu, toluene, reflux, 12 h, 83%; c) 1) 2 N HCl, THF, RT, 0.5 h; 2 N NaOH, THF, RT, 0.5 h, 97% (over two steps); d) oxalic acid, 4 N HCl, 12 h, reflux, 89%; e) thionyl chloride, DMF (cat.), 1,2-dichloroethane, reflux, 12 h, 87%.



Scheme 2. Synthesis of **MonoTriptyQxCav** and **DiTriptyQxCav**: a) Catechol (1.1 equiv), CsF, 80 °C, 1 h, 70 %; b) catechol (3.3 equiv), CsF, 80 °C, 1 h, 55 %; c) **5**, K_2CO_3, DMF, 120 °C under microwave irradiation (300 W), 1 h, 65 %.; d) **5**, K_2CO_3, DMF, 120 °C under microwave irradiation (300 W), 1 h, 46 %.

densation reaction with oxalic acid under acidic conditions to give **4**. Target 2,3-dihydroxy-6,7-triptycenequinoxaline **5** was prepared by chlorination of **4** with thionyl chloride catalyzed by DMF in refluxing 1,2-dichloroethane.

The preparation of the resorcinarene-based scaffolds required the synthesis of partially bridged triquinoxaline and diquinoxaline resorcinarenes (Scheme 2). The selective removal of one quinoxaline unit from the easily prepared **TetraQxCav** was performed by reaction with 1.1 equivalents of catechol, in the presence of cesium fluoride as base.[13] Purification by flash chromatography afforded **TriQx diol** in 70 % yield.

DiQx tetrol was prepared by selective removal of two quinoxaline units from **TetraQxCav** by using 3.3 equivalents of catechol. In the last synthetic step, the two partially bridged quinoxaline cavitands were treated with 2,3-dihydroxy-6,7-triptycenequinoxaline **5** in the presence of K_2CO_3 under microwave irradiation to afford **MonoTriptyQxCav** and **DiTriptyQxCav**. (see the Supporting Information, Figures S1–S6).

Inclusion properties in the solid state

We first determined how the presence of one and two bulky triptycene groups affects the conformation of the cavitands, and whether the vase conformation is the most stable both in solution and in the solid state. The conformational preferences of quinoxaline cavitands in solution can be deduced by ^{1}H NMR spectroscopy[3,14] through the chemical shift of the methine proton signal of the resorcinarene, which is sensitive to its orientation. Chemical shifts at around 4 ppm are characteristic of kite conformation, whereas signals shifted downfield to 5–6 ppm indicate a vase conformation. We found that both cavitands are in the vase conformation in [D_6]benzene with methine protons at $\delta = 6.0$ ppm as a broad triplet for **MonoTriptyQxCav**, and at $\delta = 6.19$ and 5.86 ppm as two sharp triplets for **DiTriptyQxCav** (see the Supporting Information, Figures S2 and S4). The vase conformation is the preferred one for both cavitands also in $CDCl_3$, where a small upfield shift of the methine protons is indicative of increased fluxionality (see the Supporting Information, Figures S1 and S3). These findings demonstrate that, despite the introduction of one or two bulky triptycene units at the upper rim, **MonoTriptyQxCav** and **DiTriptyQxCav** have an inherent preference for the vase conformation over the kite.

The crystal structures of the two cavitands confirm that the vase form also dominates in the solid state (Figure 2, see the Supporting Information for experimental details). Despite the presence of a bulky triptycene group at the upper rim of the **MonoTriptyQxCav**, the four quinoxaline substituents are almost orthogonal to the mean plane (OOp) defined by the eight oxygen atoms of the cavitand (dihedral angles range from 81 to 86°) and the cavity assumes a pseudo-fourfold-symmetric vase conformation (Figure 2 a, c).

In contrast, the presence of two encumbering triptycene groups at the upper rim of the **DiTriptyQxCav** gives rise to large distortions in the structure of the receptor and the cavity assumes a pseudo-twofold-symmetric vase conformation (Figure 2 b, d). The two opposite triptycene groups tend to repel each other because of steric hindrance: the distance between the upper border carbon atoms of the opposite quinoxaline moieties is about 10 Å, whereas the unsubstituted quinoxaline groups are at a distance of about 6 Å. The two aromatic arms bearing the triptycene groups are perpendicular to the OOp (mean value of 89°), while the pair of pure quinoxaline groups is tilted inward and forms an angle of approximately 74° with the OOp. In both crystal structures, one molecule of benzene is confined inside the cavity. In the benzene@**MonoTriptyQx-**

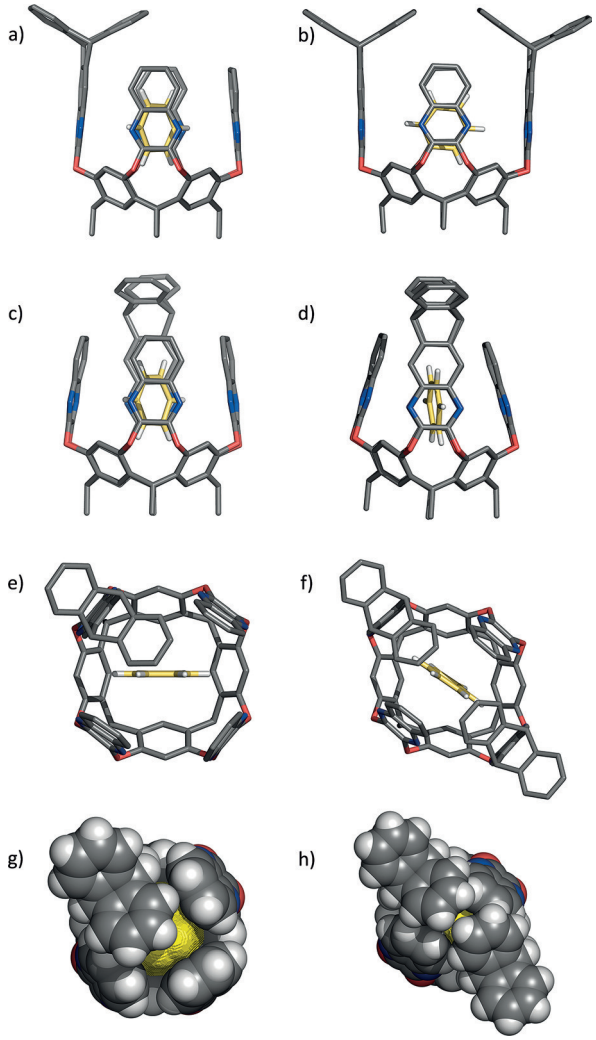


Figure 2. Side views of the crystal structures of complexes benzene@**MonoTriptyQxCav** (a,c) and benzene@**DiTriptyQxCav** (b,d) crystallized from benzene/chloroform. Solvent molecules, *n*-hexyl chains, and hydrogen atoms are omitted for clarity. Top views of benzene@**MonoTriptyQxCav** (e) and benzene@**DiTriptyQxCav** (f). Top views in space-filling models of benzene@-**MonoTriptyQxCav** (g) and benzene@**DiTriptyQxCav** (h). The surface of the void volume available inside the cavity is represented in yellow.

Cav complex, the benzene molecule is located almost at the same height as the pyrazine rings with the benzene center at 2.3 Å above the OOp. The benzene molecule is aligned in the middle of the cavity and oriented in such a way to form an angle of 45° with the four quinoxaline planes (Figure 2 e). In the benzene@**DiTriptyQxCav** complex, the benzene molecule is sandwiched between the inward-oriented quinoxaline planes (Figure 2 f). These arms clamp the benzene molecule and through the pyrazine rings form specific π–π stacking interactions. The two triptycene substituents act as a "roof", locking the entrapped benzene molecule inside the cavity. In particular, they almost completely cover the cavity (Figure 2 g, h), reducing the inner void volume from 164 $Å^3$, as calculated[15] for **MonoTriptyQxCav**, to 122 $Å^3$ for the **DiTriptyQxCav**.

The thermal stabilities of **MonoTriptyQxCav** and **DiTriptyQxCav** were measured by thermogravimetric analysis (TGA) and compared with that of the unsubstituted tetraquinoxaline cavitand (**QxCav**), used as model compound. The three receptors were dissolved in benzene and excess solvent was removed by low-pressure evaporation. The entrapped benzene guest inside the quinoxaline cavitands was only released well above its boiling point (80 °C).[16] The release temperature is a rough indication of the strength of benzene complexation: the higher the value, the stronger the host–guest interactions. The thermal behavior of the cavitands was measured under nitrogen atmosphere using temperature ramps from 20 °C to 600 °C at 5 °C min^{-1} (Figure 3).

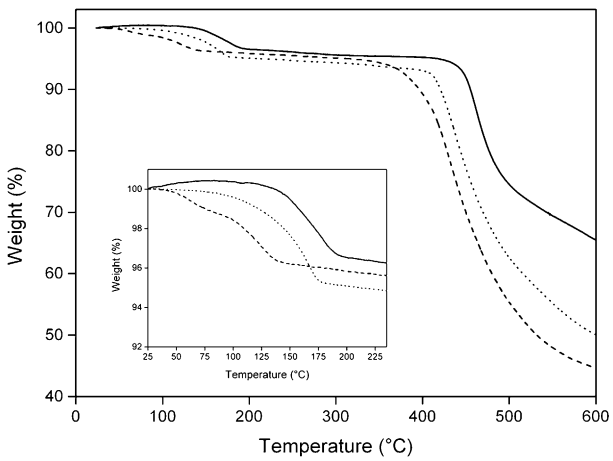


Figure 3. TGA analysis of **QxCav** (-----), **MonoTriptyQxCav** (••••) and **DiTriptyQxCav** (——) cavitands under nitrogen, with enlargement in the inset.

The three TGA traces in Figure 3 are characterized by two different weight losses due respectively to the desorption of the entrapped benzene and to the decomposition of the cavitand. The former is consistent with the theoretical mass loss resulting from decomplexation of one molecule of benzene for each cavitand (for **MonoTriptyQxCav** and **DiTriptyQxCav,** this is a mass loss of 4.93 % and 4.43 %, respectively). The presence of the triptycene roof shifts the temperature range of benzene release from the cavity up by about 50 °C as compared to **QxCav**. This shift in release temperature for both the **TriptyQxCav** species in comparison to **QxCav** is attributed to the blocking effect of the triptycene roof, which retains benzene within the cavity. The triptycene units also enhance the thermal stability of the cavitands, bringing the decomposition temperature above 400 °C.

SPME-GC-MS Analysis

The inclusion properties in the solid state of the cavitands **MonoTriptyQxCav** and **DiTriptyQxCav** were tested by SPME sampling of BTEX at trace levels in air. The fiber coatings were applied by vertically dipping the silica support of the fibers in Duralco 4460 epoxy glue and, after 2 min, in **MonoTriptyQxCav** or **DiTriptyQxCav** powders four times. Five fibers for each cavitand were prepared and tested. Experiments were carried out to select the best conditions in terms of extraction time in

the 5–20 min range. No significant differences were found between 15 and 20 min and hence 15 min was selected for BTEX extraction (see the Supporting Information, Figure S7). By operating under these conditions, the extraction capabilities of both **MonoTriptyQxCav** and **DiTriptyQxCav** cavitands were evaluated in terms of enrichment factors (EFs; Figure 4 and Table S1 in the Supporting Information).[17] EFs are 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. Experimentally, this is determined by using the ratio of the chromatographic peak area of the analyte after SPME extraction for 15 min at RT to that before extraction obtained by the direct injection of the same gas standard solution (3 replicate measurements). **DiTriptyQxCav** showed excellent enrichment capabilities, with EF values up to 9 times higher than those achieved by **MonoTriptyQxCav**. Particularly relevant for analytical purposes is the EF obtained for the carcinogenic analyte benzene, which is the highest of the entire series.

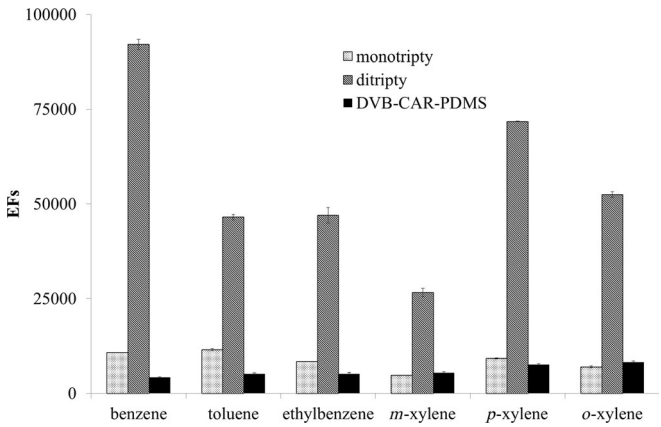


Figure 4. EFs of the **TriptyQxCav** fibers in comparison to DVB–CAR–PDMS coating for BTEX extraction. HS-SPME conditions: extraction time: 15 min, RT ($n=3$).

The enrichment capabilities of the triptycene-based SPME fibers were further compared with those of the commercial divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS) 2 cm × 50/30 μm fiber. As shown in Figure 4 by using the **DiTriptyQxCav** fiber, the enrichment factor for benzene is 22 times higher than that obtained with the commercial coating.

The selectivity of these coatings was further evaluated by sampling BTEX (3.49–4.74 $\mu g\,m^{-13}$) in the presence of much higher concentrations of aliphatic compounds (38–56 $\mu g\,m^{-13}$; Figure 5). The results revealed great differences between the desorption temperatures of BTEX and aliphatic hydrocarbons. Low temperatures (up to 75 °C) were required to completely remove the aliphatic hydrocarbons from the coating, whereas BTEX desorption began at 200 °C and was complete only at 250 °C for both cavitands. This behavior reflects the affinity of the cavity for aromatic guests, which is attributed to synergistic π–π and CH–π interactions with the walls and the bottom of the cavity.[1]

Owing to the excellent results achieved with the **DiTriptyQxCav** coating, method validation was carried out only by using this coating. Limit of detection (LOD) and limit of quantitation (LOQ) values at $ng\,m^{-3}$ levels (Table 1) proved the capabilities of the **DiTriptyQxCav** adsorbent for the determination of BTEX in air at trace levels. These values were at least 3 times lower than those achieved by using the **MonoTriptyQxCav** coating.

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

	LOD [$ng\,m^{-3}$]	LOQ [$ng\,m^{-3}$]	a[a]	b[a]
benzene	1.7	5.5	77 000 ± 1000	–[b]
toluene	3.1	10.0	55 000 ± 1700	–[b]
ethylbenzene	1.3	4.3	78 000 ± 3800	–[b]
m-xylene	2.0	6.6	72 000 ± 2200	–[b]
p-xylene	1.3	4.5	76 000 ± 2200	–[b]
o-xylene	2.2	7.3	90 000 ± 3300	–[b]

[a] Regression equation: $y=ax+b$. [b] Not significant.

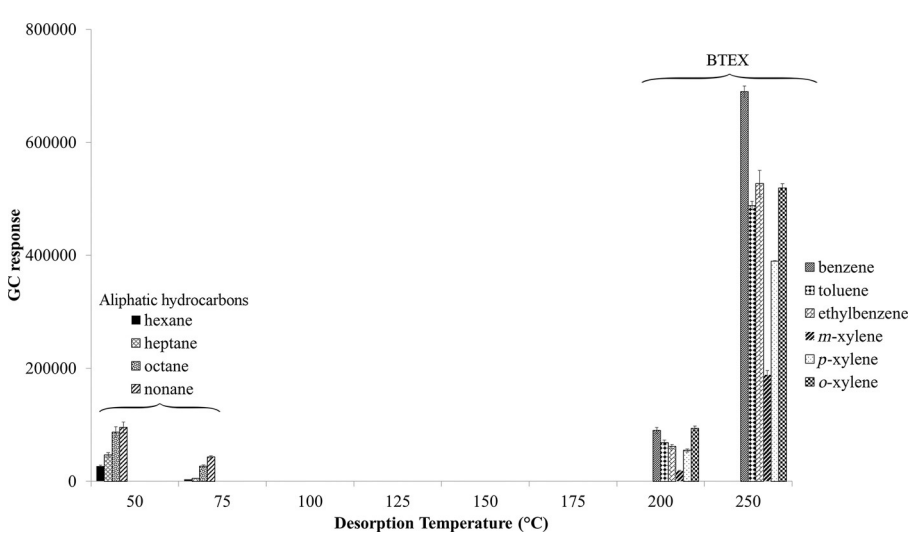


Figure 5. The desorption profile of **DiTriptyQxCav** SPME fiber upon exposure to aliphatic and aromatic hydrocarbons.

High linearity was proven for all analytes by applying Mandel's fitting test. The **DiTriptyQxCav** SPME-GC-MS method also displayed good intra-day repeatability and intermediate precision, with relative standard deviations always lower than 9%. In the case of intermediate precision, ANOVA showed that mean values were not significantly different among the 3 days, giving p values of >0.05. Extraction recoveries ranging from 97(±1)% to 107(±1)% ($n=3$) were calculated for all analytes, showing the excellent efficiency of the developed method.

Finally, the method was applied for the analysis of an environmental air sample taken at noon near a traffic fixed-site air monitoring station. The BTEX concentration levels obtained were in the 1.1–5.4 $\mu g\,m^{-3}$ range and the agreement between the results obtained by the SPME-GC-MS developed method and the data provided by the fixed-site station, confirms the suitability of the triptycene-based coating for the determination of BTEX in air.

Conclusion

Two triptycene-roofed cavitands were designed and synthesized for the detection of BTEX in air. The introduction of the triptycene units at the upper rim enforces the complexation properties towards aromatic hydrocarbons within the cavity in the solid state, and increases the temperatures required for thermal release of the trapped BTEX analytes. The best performances in terms of enrichment factors, selectivity, and LOD values were obtained by using the **DiTriptyQxCav** coating, as predicted by the crystal structures. The introduction of the second triptycene roof strengthens the binding of BTEX through additional π–π interactions induced by cavity distortion. The developed material has proved to be an excellent alternative to commercial coatings for BTEX monitoring. Moreover, this study demonstrates the importance of the supramolecular approach to solve complex analytical problems.[18]

Experimental Section

Instrumentation and materials

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Silica column chromatography was performed using silica gel 60 (Fluka 230–400 mesh or Merck 70–230 mesh). ^{1}H NMR spectra were obtained using a Bruker AVANCE 300 (300 MHz) and a Bruker AVANCE 400 (400 MHz) spectrometer at 25 °C. All chemical shifts (δ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. High-resolution MALDI-TOF was performed on an AB SCIEX MALDI TOF-TOF 4800 Plus (matrix: α-cyano-4-hydroxycinnamic acid).

Synthesis

TetraQxCav, **TriQx diol**, and **DiQx tetrol** were prepared according to a published procedure.[13]

2,3-Dibromotriptycene (1):[10] To a solution of anthracene (4 g, 22.4 mmol) and 1,2,4,5-tetrabromobenzene (12.4 g, 31.4 mmol) in dry toluene (100 mL), *n*BuLi (2.5 M solution in hexane, 14.36 mL, 35.9 mmol) diluted in hexane (50 mL) was slowly added under argon atmosphere at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction mixture was filtered and the removed solid was washed with dichloromethane and hexane (50 mL + 50 mL). Solvents were removed under reduced pressure. Purification of the residue by silica gel column chromatography (hexane as eluent) afforded the pure product as white solid (5.7 g, 13.9 mmol, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=7.63$ (s, 2H, Ar*H*), 7.39–7.36 (m, 4H, Ar*H*), 7.04–7.01 (m, 4H, Ar*H*), 5.36 (s, 2H, Ar*CH*).

2,3-Bis(diphenyldiiminotriptycene) (2): A solution of tris(dibenzylideneacetone)dipalladium(0) (0.36 g, 0.39 mmol) and (±)-BINAP (0.49 g, 0.79 mmol) in toluene (50 mL) was degassed 3 times by freeze-pump-thaw technique, purged with argon and stirred at 110 °C for 1 h. The solution was cooled down to room temperature and benzophenone imine (2.13 mL, 10.9 mmol), 2,3-dibromotriptycene **1** (2 g, 4.85 mmol) and sodium *tert*-butoxide (1.22 g, 12.7 mmol) were added. The reaction mixture was stirred overnight at 110 °C. The reaction mixture was filtered and the formed precipitate was washed with dichloromethane (40 mL). Solvents were removed under reduced pressure. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate 9:1) afforded pure **2** as a yellow solid (2.46 g, 4.01 mmol, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.61$ (d, $J=7$ Hz, 4H, ArH_o), 7.40–7.36 (m, 2H, ArH_p), 7.32–7.30 (m, 4H, ArH_m), 7.26–7.24 (m, 4H, triptycene Ar*H*), 7.22–7.20 (m, 2H, ArH_p), 7.10 (t, $J=8$ Hz, 4H, ArH_m), 6.99–6.95 (m, 4H, triptycene Ar*H*), 6.98 (d, $J=7$ Hz, 4H, ArH_o), 6.55 (s, 2H, triptycene Ar*H*), 5.07 (s, 2H, Ar*CH*).

2,3-Diaminotriptycene (3): A 2 M aqueous HCl solution (5.1 mL, 10.2 mmol) was added to a solution of **2** (2.1 g, 3.41 mmol) in THF (50 mL) and the mixture was stirred at room temperature for 0.5 h. The resultant precipitate was isolated by filtration, sonicated in dichloromethane (50 mL) for 0.5 h and filtered again to give the diammoniumtriptycene dichloride salt as an off-white solid. Neutralization was carried out by stirring a suspension of the salt (1.21 g, 3.39 mmol) in THF (50 mL) with 2.0 M aqueous NaOH solution (2.5 mL, 5.0 mmol) at room temperature for 0.5 h. Solvent was evaporated under reduced pressure to give **3** as a yellow solid (0.94 g, 3.31 mmol, 97%). ^{1}H NMR ([D_6]DMSO, 400 MHz): $\delta=7.32$–7.29 (m, 4H, Ar*H*), 6.92–6.89 (m, 4H, Ar*H*), 6.61 (s, 2H, Ar*H*), 5.22 (s, 2H, Ar*CH*).

2,3-Dihydroxy-6,7-triptycenequinoxaline (4): A solution of oxalic acid (0.3 g, 3.52 mmol) in 4 N HCl (5 mL) was added to a solution of **3** (0.77 g, 2.71 mmol) in 4 N HCl (15 mL), and the resulting solution was heated at reflux overnight. The reaction mixture was cooled to room temperature, and the precipitate was isolated by filtration, washed with water (20 mL) and dried to afford **4** as a brown solid (0.82 g, 2.41 mmol, 89%). ^{1}H NMR ([D_6]DMSO, 400 MHz): $\delta=11.88$ (s, 2H, Ar*OH*), 7.43–7.37 (m, 4H, Ar*H*), 7.16 (s, 2H, Ar*H*), 6.98–6.95 (m, 4H, Ar*H*), 5.61 (s, 2H, Ar*CH*).

2,3-Dihydroxy-6,7-triptycenequinoxaline (5): To a suspension of **4** (0.62 g, 1.83 mmol) and thionyl chloride (0.345 mL, 4.76 mmol) in 1,2-dichloroethane (40 mL), a few drops of DMF were added. The reaction mixture was heated at reflux overnight. Solvent was removed under reduced pressure and the crude was purified by silica flash chromatography (hexane/ethyl acetate 9:1) to give **5** as a white solid (0.6 g, 1.59 mmol, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=$

7.91 (s, 2H, Ar*H*), 7.49–7.46 (m, 4H, Ar*H*), 7.11–7.06 (m, 4H, Ar*H*), 5.64 (s, 2H, Ar*CH*); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 148.4$, 143.5, 139.7, 126.3, 124.4, 121.9, 53.8.

MonotriptyQxCav: To a solution of **TriQx diol** (0.18 g, 0.15 mmol) in dry DMF (5 mL) in an oven-dried microwave vessel, K_2CO_3 (0.082 g, 0.60 mmol) was added. The resulting mixture was stirred for 15 min at room temperature under argon atmosphere, followed by addition of **5** (0.061 g, 0.16 mmol). The mixture reaction was stirred at 120 °C under microwave irradiation for 1 h. The reaction was quenched by addition of 1 N HCl (5 mL) and the precipitate was filtered, washed with water (5 mL), and dried. The crude product was purified by flash column chromatography (dichloromethane as eluent) to give **MonoTriptyQxCav** as a white solid (0.16 g, 0.10 mmol, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.02$ (s, 2H), 7.99 (s, 2H), 7.95 (d, 2H, $J = 7.8$ Hz), 7.86 (d, 2H, $J = 7.8$ Hz), 7.75–7.72 (m, 2H), 7.65 (s, 2H), 7.63–7.57 (m, 4H), 7.47 (bs, 4H), 7.33–7.30 (m, 2H), 7.15 (s, 2H), 7.13 (s, 2H), 7.08–7.05 (s, 2H), 7.03–7.00 (m, 2H), 5.43 (s, 2H), 5.34 (t, 3H, $J = 8.1$ Hz), 5.25 (t, 1H, $J = 7.9$ Hz), 2.24–2.19 (m, 8H), 1.45–1.26 (m, 32H), 0.93–0.87 (m, 12H; see the Supporting Information for signal assignment); MALDI TOF: calculated for $C_{98}H_{88}N_8O_8$ $[M+H]^+$ *m/z*: 1505.680, found *m/z* = 1505.691.

DitriptyQxCav: To a solution of **DiQx tetrol** (0.1 g, 0.09 mmol) in dry DMF (5 mL) in an oven-dried microwave vessel, K_2CO_3 (0.102 g, 0.74 mmol) was added. The resulting mixture was stirred for 15 min at room temperature under argon atmosphere, followed by addition of **5** (0.076 g, 0.20 mmol). The mixture reaction was stirred at 120 °C under microwave irradiation for 1 h. The reaction was quenched by addition of 1 N HCl (5 mL) and the precipitate was filtered, washed with water (5 mL), and dried. The crude product was purified by flash column chromatography (dichloromethane as eluent) to give **11** as a white solid (0.072 g, 0.04 mmol, 46%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.87$ (s, 4H), 7.76 (s, 4H), 7.73–7.70 (m, 4H), 7.50–7.47 (m, 8H), 7.28–7.26 (m, 4H), 7.15–7.13 (m, 4H), 7.09–7.07 (m, 4H), 7.00 (s, 4H), 5.62 (s, 4H), 4.86–4.81 (m, 4H), 2.20–2.04 (m, 8H), 1.43–1.20 (m, 32H), 0.89–0.83 (m, 12H; see the Supporting Information for signal assignment); MALDI TOF: calculated for $C_{112}H_{96}N_8O_8$ $[M+H]^+$ *m/z:* 1681.743, found *m/z* = 1681.744.

SPME-GC-MS analysis

All SPME experiments were performed by using a CTC CombiPAL autosampler (CTC Analyticas, Zwingen, Switzerland). Prior to use, all fibers were conditioned in the GC injection port at 300 °C for 1 h under a helium flow. Air sampling of BTEX was performed by exposing the SPME fibers in an air atmosphere containing a mixture of both aromatic and aliphatic (C_6 to C_9) compounds (BTEX: 3.49 $\mu g\,m^{-13}$–4.74 $\mu g\,m^{-13}$ range; aliphatic hydrocarbons: 38–56 $\mu g\,m^{-13}$ range). Benzene and ethylbenzene (99.8 and 99.5% purity, respectively) were from Carlo Erba (Milano, Italy). *n*-Pentane and *n*-nonane (both 99% purity), methanol and toluene (both 99.9% purity), *n*-hexane (97% purity), and *n*-octane (98% purity) were from Sigma–Aldrich (Milan, Italy). N-heptane (95% purity) was provided by Lab-Scan (Dublin, Ireland), *m*-xylene, *p*- and *o*-xylene (all 98% purity) were from Fluka (Milan, Italy). SPME bare fused silica fibers and commercial fibers [Carboxen–PDMS (CAR–PDMS) 75 μm and DVB–CAR–PDMS 2 cm × 50/30 μm] were purchased from Supelco (Bellefonte, PA, USA). Duralco 4460 epoxy glue was provided by Cotronics Corp. (Brooklyn, NY, USA).

The extraction was carried out at room temperature for 15 min. A HP 6890 Series Plus gas chromatograph (Agilent Technologies, Palo Alto, CA) equipped with a MSD 5973 mass spectrometer (Agilent Technologies) was applied. 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 a 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 × 0.25 mm, df 0.25 μm HP-5 ms capillary column (Agilent Technologies). The transfer line and source were maintained at the temperatures of 220 °C and 150 °C, respectively. Preliminarily, full scan EI data were acquired to determine appropriate masses for selected-ion monitoring mode (*m/z* 78 and 56 for 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 by using HP Chemstation (Agilent Technologies). The performance of different fibers was compared: mono- and ditriptycene and DVB–CAR–PDMS 2 cm × 50/30 μm (Supelco).

Method validation

Method validation was performed according to EURACHEM guidelines[19] by calculating the following parameters: detection and quantitation limit, linearity, precision, and trueness.[20] Linearity was evaluated on six concentration levels in the LOQ-3500 ng m^{-3} for benzene, LOQ-4100 ng m^{-3} for toluene, LOQ-4700 ng m^{-3} for ethylbenzene, *m-*, *p-*, and *o*-xylenes. Three replicated measurements for each level were performed. Method precision was evaluated both in terms of intra-day and intermediate precision testing at two concentration levels, that is, LOQ and the upper level of the calibration range for all analytes. Trueness was assessed in terms of recovery rate at the same concentration levels used for the evaluation of precision.

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