# Supporting Information

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

Federico Bertani,[a, b] Nicolò Riboni,[a] Federica Bianchi,[a] Giovanna Brancatelli,[c] Elizabeth S. Sterner,[b] Roberta Pinalli,[a] Silvano Geremia,[c] Timothy M. Swager,*[b] and Enrico Dalcanale*[a]

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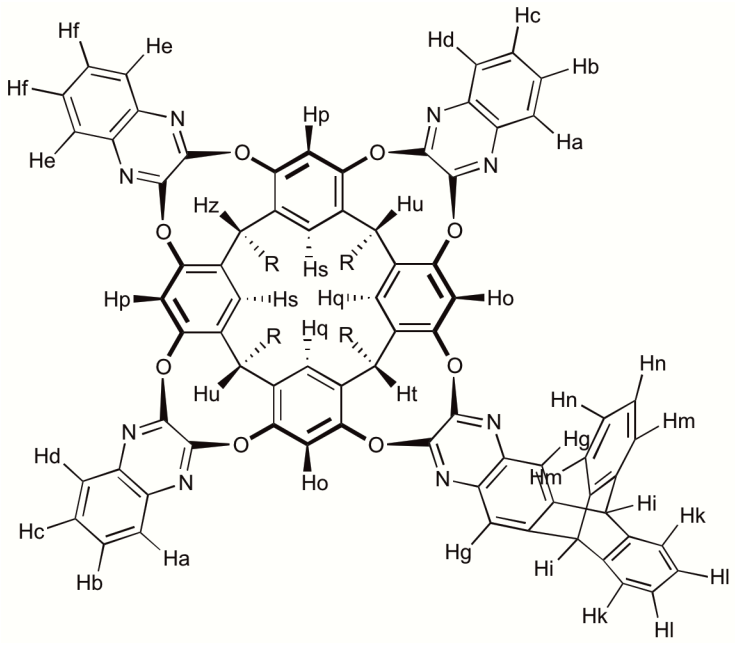
# $^1$H NMR Signals assignments

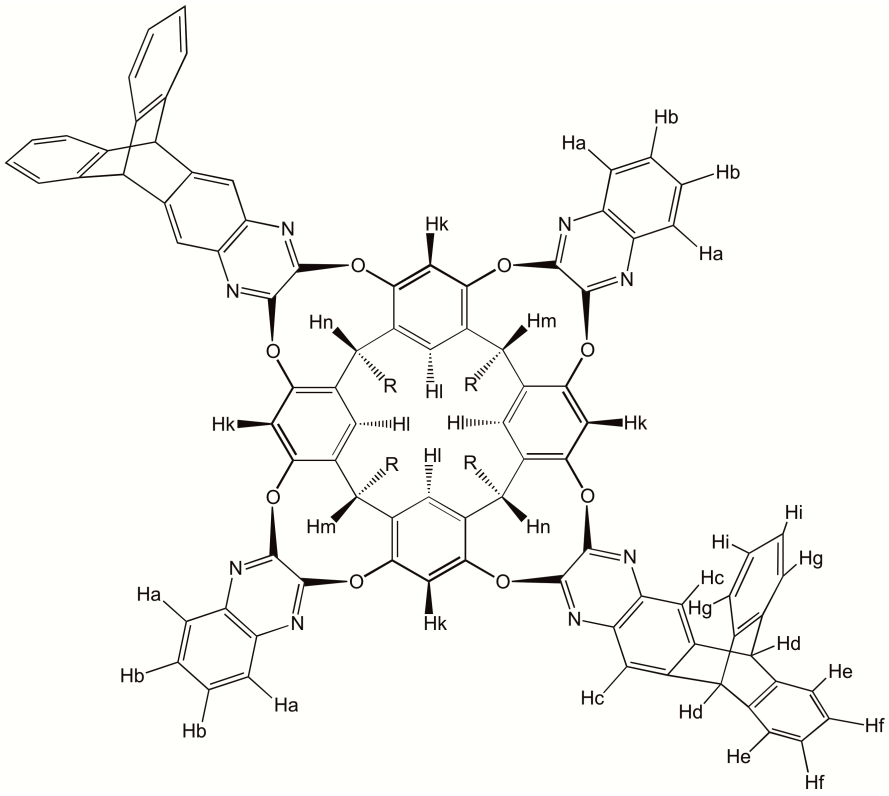
**MonoTriptyQxCav**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 8.02 (s, 2H, Hp), 7.99 (s, 2H, Ho), 7.95 (d, 2H, J=7.8 Hz, Hd), 7.86 (d, 2H, J=7.8 Hz, Ha), 7.75-7.72 (m, 2H, He), 7.65 (s, 2H, Hg), 7.63-7.57 (m, 4H, Hb+Hc), 7.47 (bs, 4H, Hf+Hk), 7.33-7.30 (m, 2H, Hm), 7.15 (s, 2H, Hs), 7.13 (s, 2H, Hq), 7.08-7.05 (s, 2H, Hl), 7.03-7.00 (m, 2H, Hn), 5.43 (s, 2H, Hi), 5.34 (t, 3H, J=8.1 Hz, Hu+Hz), 5.25 (t, 1H, J=7.9 Hz, Ht), 2.24-2.19 (m, 8H, CHC**H$_2$**CH$_2$), 1.45-1.26 (m, 32H, -C**H$_2$**-), 0.93-0.87 (m, 12H, $CH_2CH_2$**C$H_3$**) (Assignment by COSY NMR).



**DitriptyQxCav**

**$^1$H NMR** ($CDCl_3$, 400 MHz): δ = 7.87 (s, 4H, Hl), 7.76 (s, 4H, Hc), 7.73-7.70 (m, 4H, Ha), 7.50-7.47 (m, 8H, Hg+He), 7.28-7.26 (m, 4H, Hb), 7.15-7.13 (m, 4H, Hf), 7.09-7.07 (m, 4H, Hi), 7.00 (s, 4H, Hk), 5.62 (s, 4H, Hd), 4.86-4.81 (m, 4H, Hn+Hm), 2.20-2.04 (m, 8H, CHC**H$_2$**CH$_2$), 1.43-1.20 (m, 32H, -C**H$_2$**-), 0.89-0.83 (m, 12H, CH$_2$CH$_2$**CH$_3$**), (Assignment by COSY NMR).



## $^1$H NMR Spectra of MonoTriptyQxCav

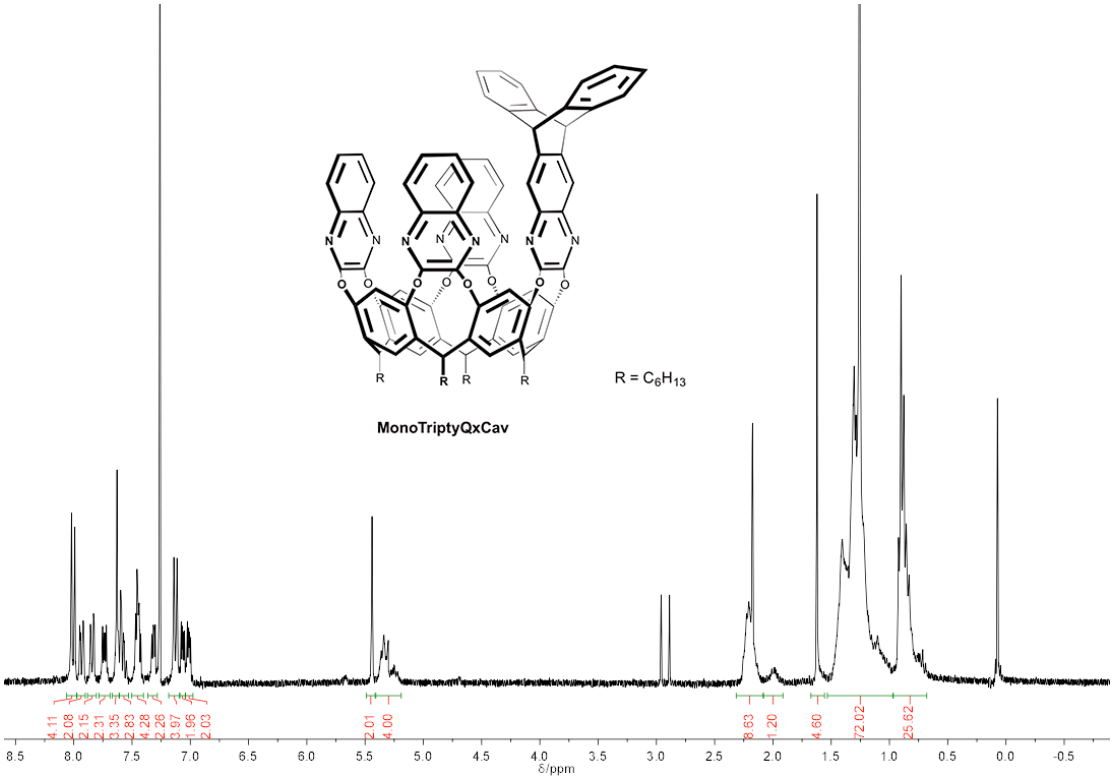



**Figure S1** $^1$H NMR (400 MHz) spectrum of **MonoTriptyQxCav** in $CDCl_3$ at 298 K.

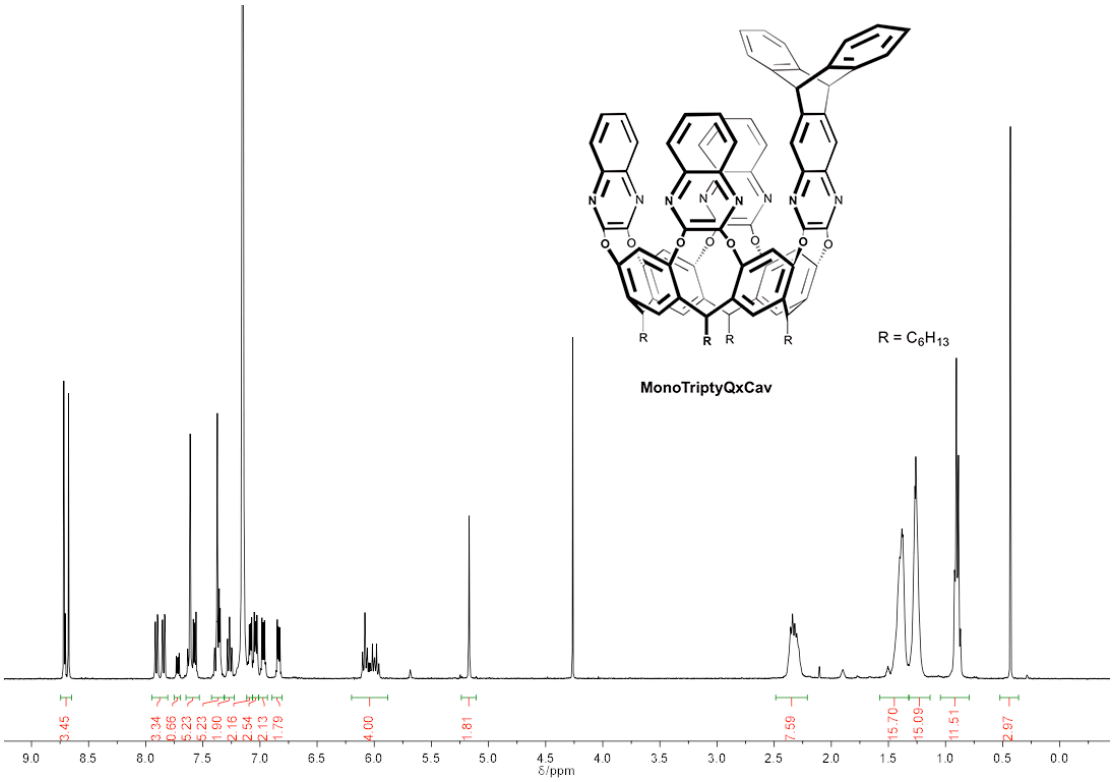



**Figure S2** $^1$H NMR (400 MHz) spectrum of **MonoTriptyQxCav** in $C_6D_6$ at 298 K.

## $^{1}$H NMR Spectra of DiTriptyQxCav

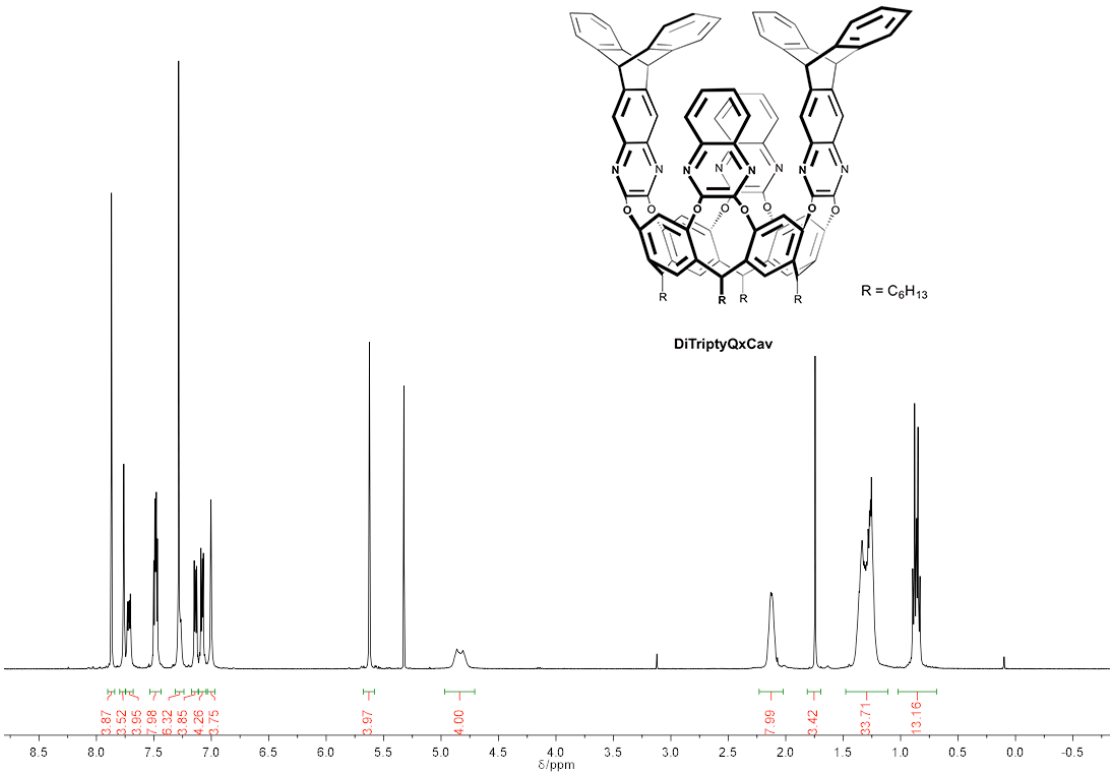



**Figure S3** $^{1}$H NMR (400 MHz) spectrum of **DiTriptyQxCav** in $CDCl_3$ at 298 K.

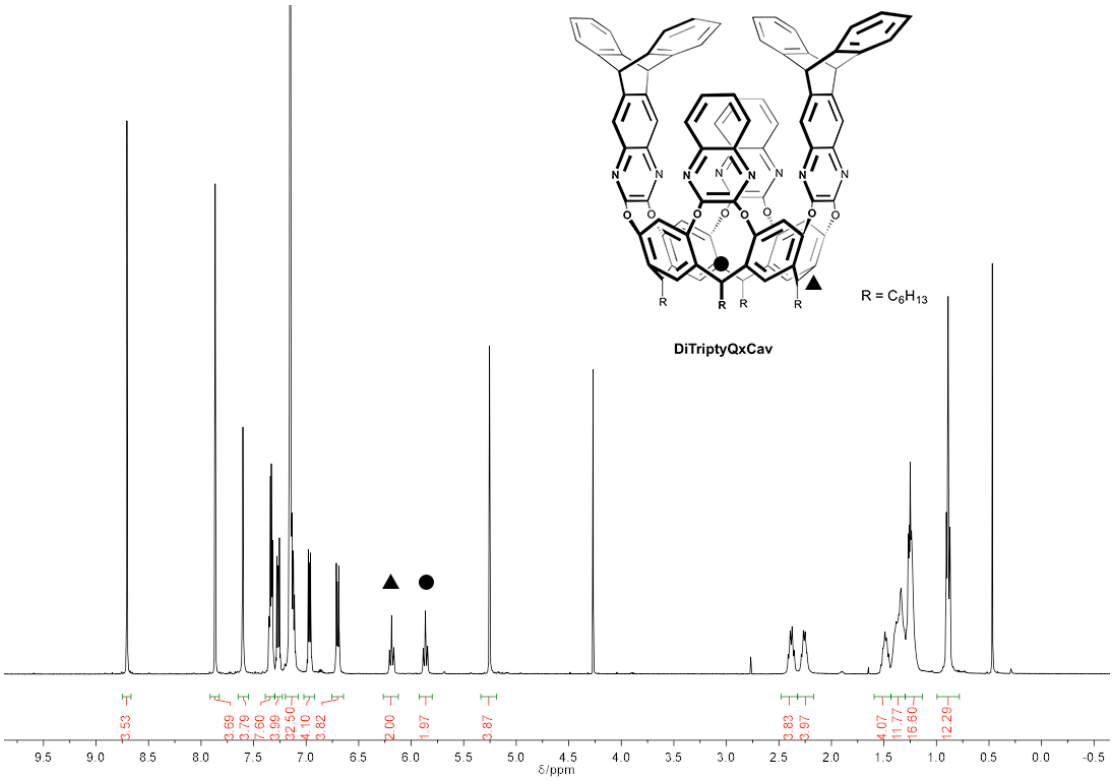



**Figure S4** $^{1}$H NMR (400 MHz) spectrum of **DiTriptyQxCav** in $C_6D_6$ at 298 K.

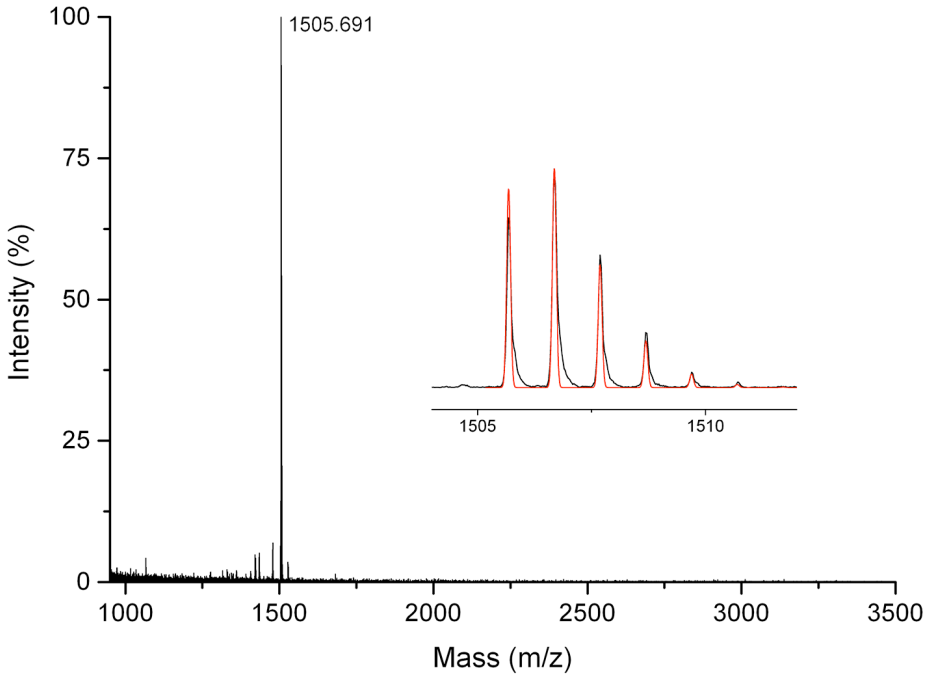



**Figure S5** High-resolution MALDI-TOF spectrum of **MonoTriptyQxCav**, with experimental (black lines) versus theoretical (red) isotopic distribution pattern in the inset.

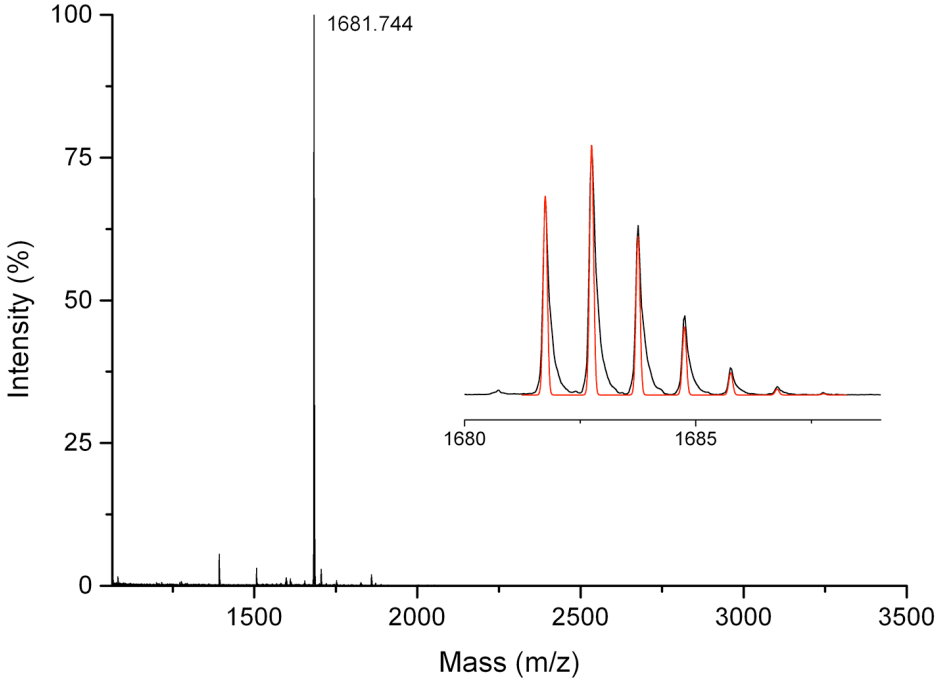



**Figure S6** High-resolution MALDI-TOF spectrum of **DiTriptyQxCav**, with experimental (black lines) versus theoretical (red) isotopic distribution pattern in the inset.

**SPME-GC-MS Analysis**

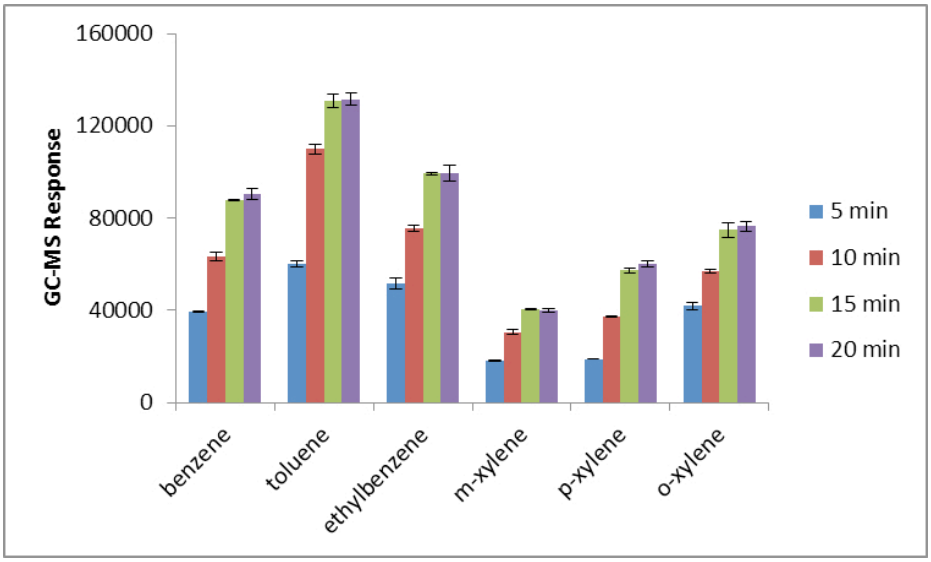



**Figure S7** SPME-GC-MS response with different extraction times.

| Analyte | MonoTriptyQxCav | DiTriptyQxCav |
|---|---|---|
| benzene | 10700±100 | 92000±2600 |
| toluene | 12000±550 | 46000±1400 |
| ethylbenzene | 8300±70 | 47000±4100 |
| *m*-xylene | 4800±80 | 27000±2300 |
| *p*-xylene | 9200±300 | 71700±200 |
| *o*-xylene | 6900±600 | 52000±1600 |

**Table S1** EFs of the TriptyQxCav-fibers. HS-SPME conditions: extraction time: 15 min, RT (n=3).

**Crystallographic determination of benzene@MonoTriptyQxCav and benzene@ DiTriptyQxCav complexes**

Crystals of compounds **benzene@MonoTriptyQxCav** and **benzene@ DiTriptyQxCav** were analyzed by single-crystal X-ray diffraction. Data collections were carried out at the Elettra synchrotron (Trieste, Italy), by using cryo-cooling techniques. In particular data collection for compound **benzene@MonoTriptyQxCav** was very challenging, because the crystals were very thin platelets and showed high anisotropy in X-ray diffraction. In particular, when the platelets were parallel to the primary beam the diffraction intensities decreased dramatically. Furthermore, the stuck flat crystals did not permit to collect a clear diffraction pattern from a single crystal. Several data sets were collected and by merging two of them by AIMLESS[1] it was possible to obtain a complete data set at 1 Å of resolution.

Both crystal structures were solved by Direct Methods with the SIR2014[2] software and refined with SHELX-13[3]. Crystallographic details are reported in Table S2.

In the asymmetric unit of **benzene@DiTriptyQxCav** three crystallographic independent cavitands were found. Each one hosts a molecule of benzene, except for one where the cavity binding site is shared by a benzene molecule and a $CHCl_3$ with partial occupancy of 83 and 17%, respectively. Two alkyl chains at the lower rim of two cavitands were found disordered over two orientations refined at 55/45% and 60/40% of partial occupancy, respectively.

**Table S1.** Crystallographic data and refinement details for crystals of **benzene@MonoTriptyQxCav** and **benzene@DiTriptyQxCav**.

| | **benzene@MonoTriptyQxCav** | **benzene@DiTriptyQxCav** |
|---|---|---|
| Empirical formula | $C_{98}H_{88}N_8O_8$, $C_6H_6$ | 2($C_{112}H_{96}N_8O_8$, $C_6H_6$), ($C_{112}H_{96}N_8O_8$, 0.83 $C_6H_6$, 0.17 $CHCl_3$) |
| Formula weight | 1583.87 | 5287.16 |
| $T$ (K) | 100(2) | 100(2) |
| $\lambda$ (Å) | 0.88 | 0.850 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P$ -1 |
| Unit cell dimensions (Å, °) | $a$ = 12.394(2), $\alpha$ = 90 | $a$ = 20.75(2), $\alpha$ = 88.39(5) |
| | $b$ = 18.561(3), $\beta$ = 96.41(2) | $b$ = 25.25(2), $\beta$ = 102.35(5) |
| | $c$ = 37.191(4), $\gamma$ = 90 | $c$ = 28.81(2), $\gamma$ = 107.28(5) |
| $V$ (Å$^3$) | 8502(2) | 14070(19) |
| $Z$ | 4 | 2 |
| $\rho_{(calc)}$ (g/mm$^3$) | 1.237 | 1.248 |
| $\mu$ (mm$^{-1}$) | 0.126 | 0.123 |
| F(000) | 3352 | 5585 |
| Resolution limits (Å) | 18.55-1.00 | 28.12-0.87 |
| Data / restraints / parameters | 9681 / 66 / 1077 | 38534 / 0 / 3657 |
| $R_1$, $wR_2$ [I > 2σ(I)] | 0.1612, 0.4233 | 0.1032, 0.2660 |
| $R_1$, $wR_2$ (all data) | 0.2092, 0.4536 | 0.1186, 0.2784 |
| GooF | 1.027 | 1.099 |
| CCDC code | 1428158 | 1427222 |

**References**

[1] a) P. R. Evans, *Acta Crystallogr*. **2006**, *D62*, 72-82; b) M. D. Winn, C. C. Ballard, K. D. Cowtan, E. J. Dodson, P. Emsley, P. R. Evans, R. M. Keegan, E. B. Krissinel, A. G. W. Leslie, A. McCoy, S. J. McNicholas, G. N. Murshudov, N. S. Pannu, E. A. Potterton, H. R. Powell, R. J. Read, A. Vagin, K. S. Wilson, *Acta. Crystallogr*. **2011**, *D67*, 235-242.

[2] M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, *J. Appl. Crystallogr*. **2015**, *48*, 306-309.

[3] G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122.