

Cite this article: Smith R, Vitorica-Yrezabal IJ, Hill A, Brammer L. 2017 Arene guest selectivity and pore flexibility in a metal–organic framework with semi-fluorinated channel walls. *Phil. Trans. R. Soc. A* **375**:20160031. <http://dx.doi.org/10.1098/rsta.2016.0031>

Guest-exchange and pore flexibility in a MOF with semi-fluorinated channel walls

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1. Crystal Structure of **1**

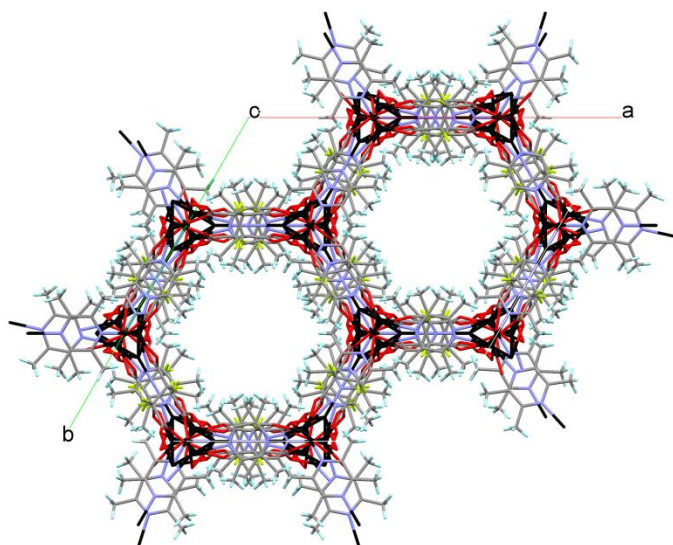


Figure S1. (a) Crystal structure of **1** viewed down *c*-axis showing hexagonal channels. Silver atoms in black, carbon in grey, hydrogen in cyan, nitrogen in blue, fluorine in yellow.

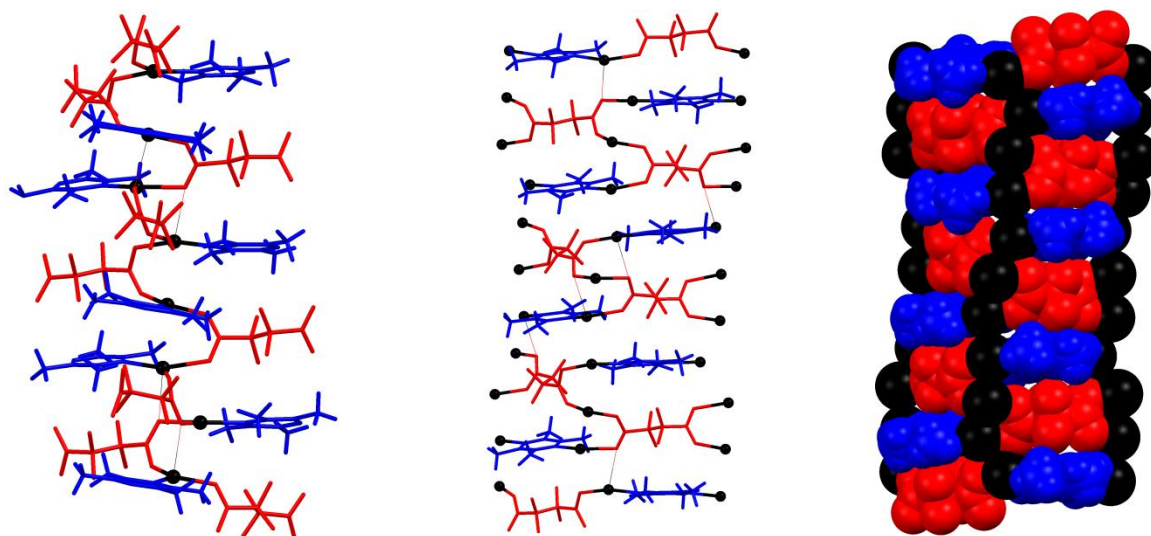


Figure S2. (a) A section of the column of Ag(I) centres that lies along the intersection of channel walls (along *c*-axis) in **1** showing the trigonal (and occasional pseudotetrahedral) coordination of Ag(I) centres. (b) Section showing two walls of a channel emphasising alternating arrangement of ligands. (c) Same section as shown in (b), but in spacefilling representation to illustrate rugose channel wall surfaces. Long Ag–O bonds (2.696 Å) are shown thin lines. Ag atoms in black, tetrafluorosuccinate ligands in red, TMP ligands in blue.

2. Guest exchange

$[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{MeOH})_x(\text{guest})_y$, (guest = toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,4,5-tetramethylbenzene, 1,2,4,5-tetrafluorobenzene, pentane, cyclohexane and perfluoro(methylcyclohexane))

Crystals of **1-MeOH** were prepared in methanol as described in the Experimental section. The methanol was then decanted and 10 mL of the required guest added (all guests are liquid at room

temperature except for tetramethylbenzene, for which a saturated solution of tetramethylbenzene in toluene was prepared instead). After 24 h the guest solutions were decanted again and replaced with another 10 mL of guest solution and left for a further 24 h. Samples were then analysed by TGA and ^{13}C CP-MAS solid-state NMR spectroscopy. After digestion of the MOF in DMSO, analysis of guest content by solution-phase ^1H NMR spectroscopy and gas chromatography was conducted.

3. Thermogravimetric Analysis Data

Thermogravimetric analyses were conducted using a Perkin-Elmer Pyris1 TGA model thermogravimetric analyser. Samples were heated from 25 to 450 °C at 5 °C min $^{-1}$, under a nitrogen atmosphere.

[Ag₂(O₂CCF₂CF₂CO₂)(TMP)] (1)

Thermogravimetric analysis was conducted on a dry sample of **1** to determine the stability of the framework and how it degrades upon increasing the temperature to 450 °C. There is a mass loss of approximately 24.9% with an onset temperature of around 160 °C which corresponds to the loss of tmp (expected 25.2%) leaving [Ag₂{O₂C(CF₂)₂CO₂}}]. From 330 °C there is another mass loss of 34.6% corresponding to the loss of tetrafluorosuccinate (expected 35.19%) to leave Ag₂O.

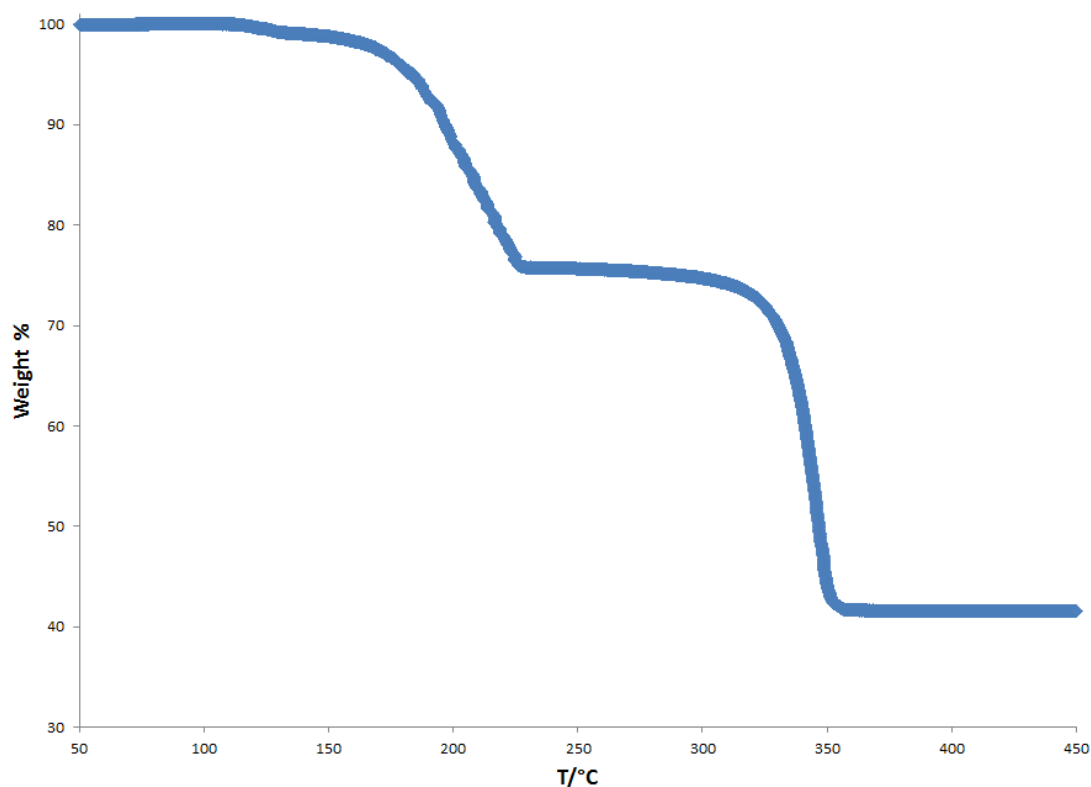


Figure S3. TGA trace for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]

[Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(toluene)_x

A sample of [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(toluene)_x was heated to 300 °C to determine the relative proportion of toluene and TMP in the material. There is a mass loss of around 7.4% between 110 °C-140 °C assigned to toluene and a further loss of 22.6 % in the temperature range 160–240 °C caused by TMP (expected 23.4%) leaving [Ag₂{O₂C(CF₂)₂CO₂}}]. This suggests there are approximately 0.4 toluene molecules per formula unit.

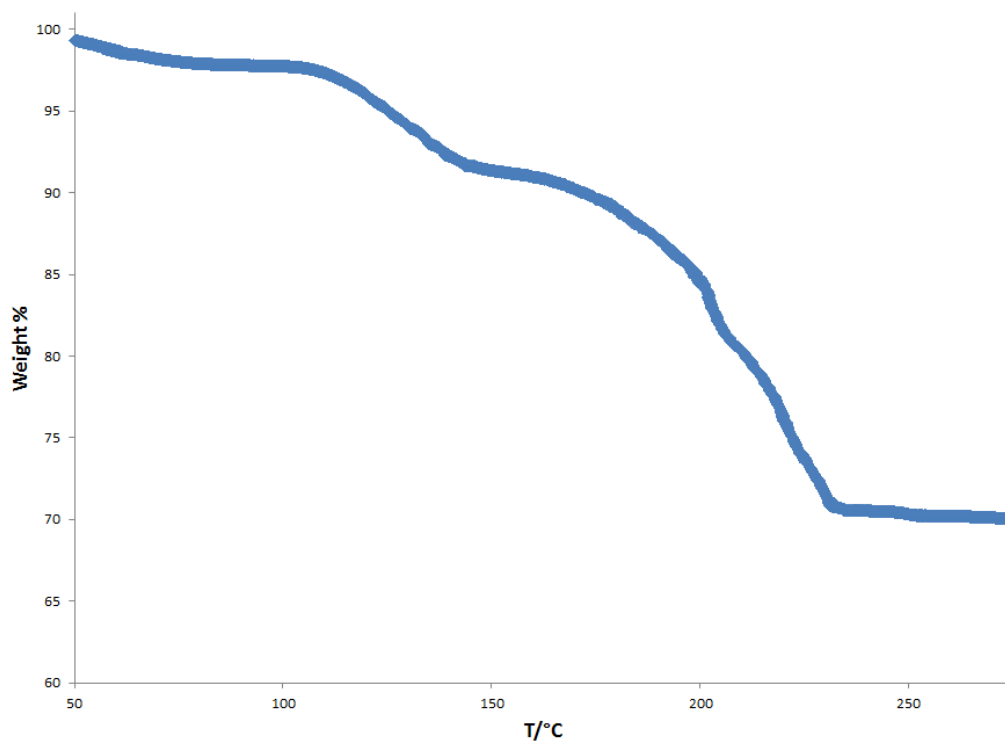


Figure S4. TGA trace for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{toluene})_x$

$[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (m\text{-xylene})_x$

A sample of $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (m\text{-xylene})_x$ was heated to 300 °C to determine the relative proportion of *m*-xylene and tmp in the material. There is a mass loss of around 8.3% in the temperature range 110–140 °C assigned to *m*-xylene and a further loss of 23.6 % in the temperature range 150–240 °C caused by TMP (expected 22.9 %) leaving $[\text{Ag}_2\{\text{O}_2\text{C}(\text{CF}_2)_2\text{CO}_2\}]$. This suggests there are approximately 0.46 *m*-xylene molecules per formula unit.

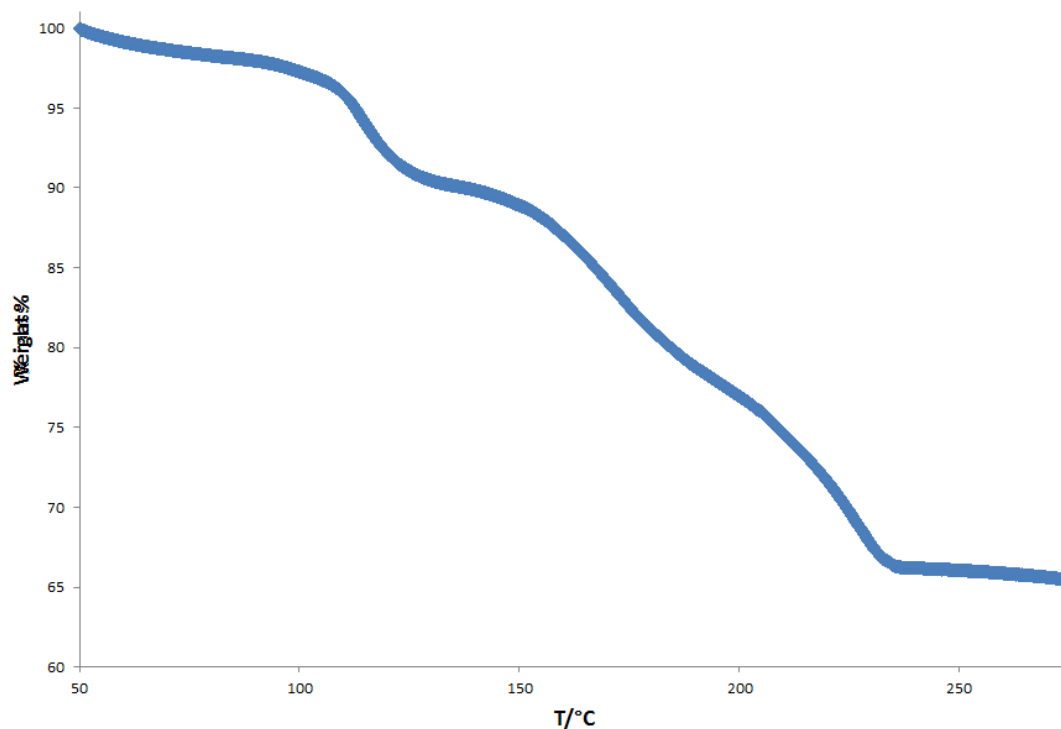


Figure S5. TGA trace for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (m\text{-xylene})_x$

$[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (p\text{-xylene})_x$

A sample of $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (p\text{-xylene})_x$ was heated to 300 °C to determine the relative proportion of *m*-xylene and tmp in the material. There is a mass loss of around 4.6 % in the temperature range 120–160 °C assigned to *p*-xylene and a further loss of 23.0 % in the temperature range 160–240 °C caused by TMP (expected 23.1 %) leaving $[\text{Ag}_2\{\text{O}_2\text{C}(\text{CF}_2)_2\text{CO}_2\}]$. This suggests there are approximately 0.24 *p*-xylene molecules per formula unit.

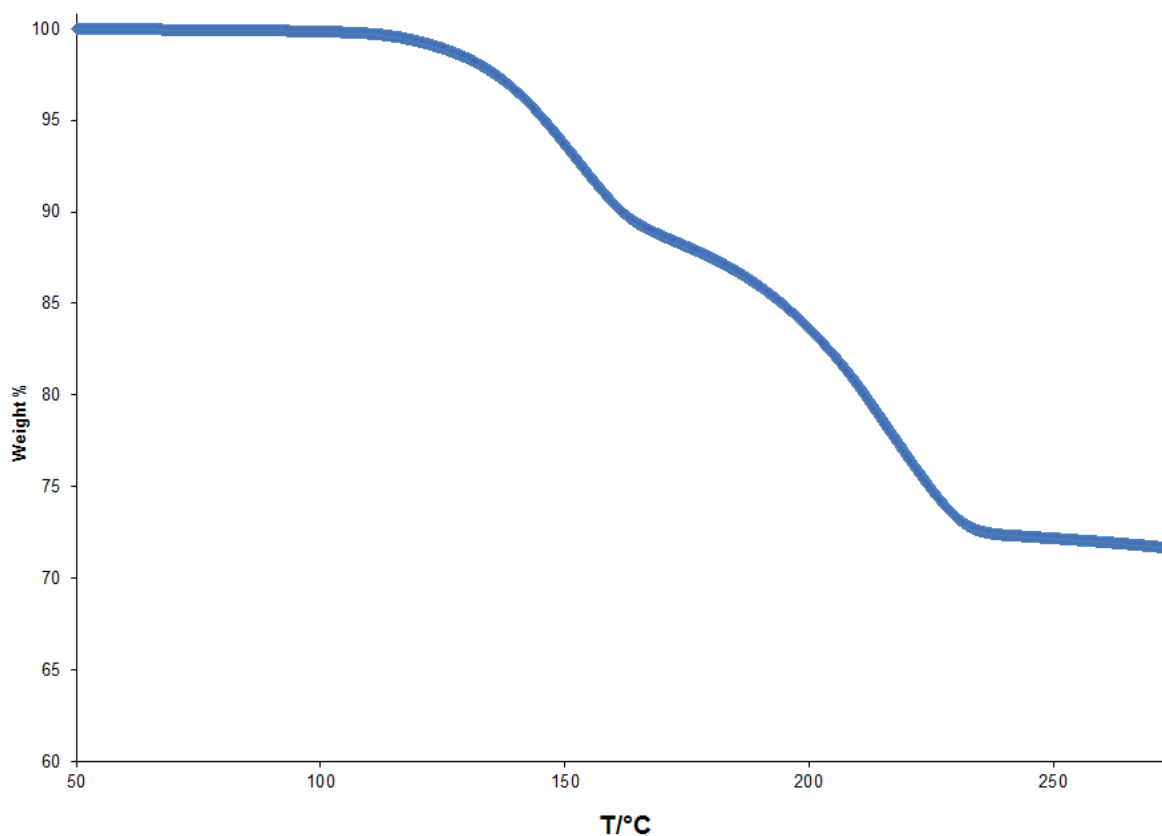


Figure S6. TGA trace for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (p\text{-xylene})_x$

$[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (o\text{-xylene})_x$

A sample of $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (o\text{-xylene})_x$ was heated to 300 °C to determine the relative proportion of *o*-xylene and TMP in the material. There is a mass loss of around 8.3 % in the temperature range 110–140 °C assigned to *o*-xylene and a further loss of 22.5 % in the temperature range 160–240 °C caused by TMP (expected 22.2 %) leaving $[\text{Ag}_2\{\text{O}_2\text{C}(\text{CF}_2)_2\text{CO}_2\}]$. This suggests there are approximately 0.46 *o*-xylene molecules per formula unit.

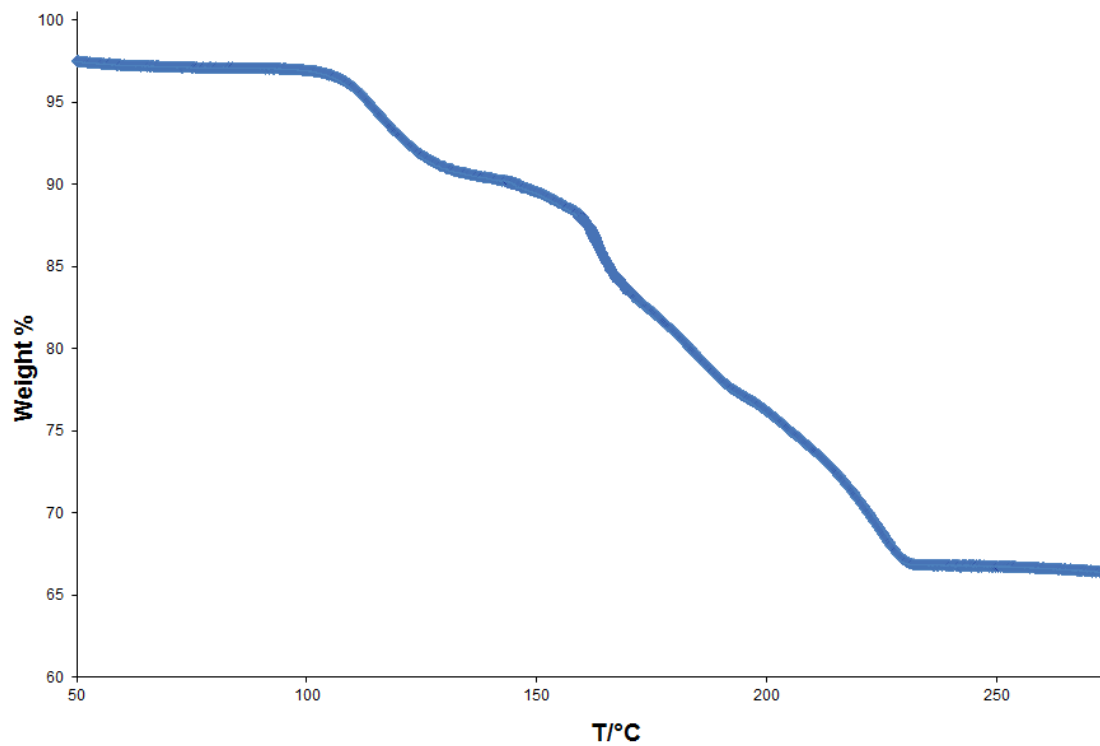


Figure S7. TGA trace for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{o-xylene})_x$

4. ^{13}C solid-state NMR Spectroscopic Data

^{13}C NMR spectra were recorded on a Bruker 500 MHz FT-NMR spectrometer (125.669 MHz for ^{13}C). All experiments used cross-polarisation from ^1H and magic angle spinning at 8–10 Hz. Data were processed using Bruker TOPSPIN 1.3 and MestRe Nova. All chemical shifts were referenced to a solid sample of adamantane.

Aug18
Rebecca Smith Sample Ref:
13C{1H} CP-TOSS @ 8 kHz (cnst31)
d1=2s, ns=2k, p15=2ms

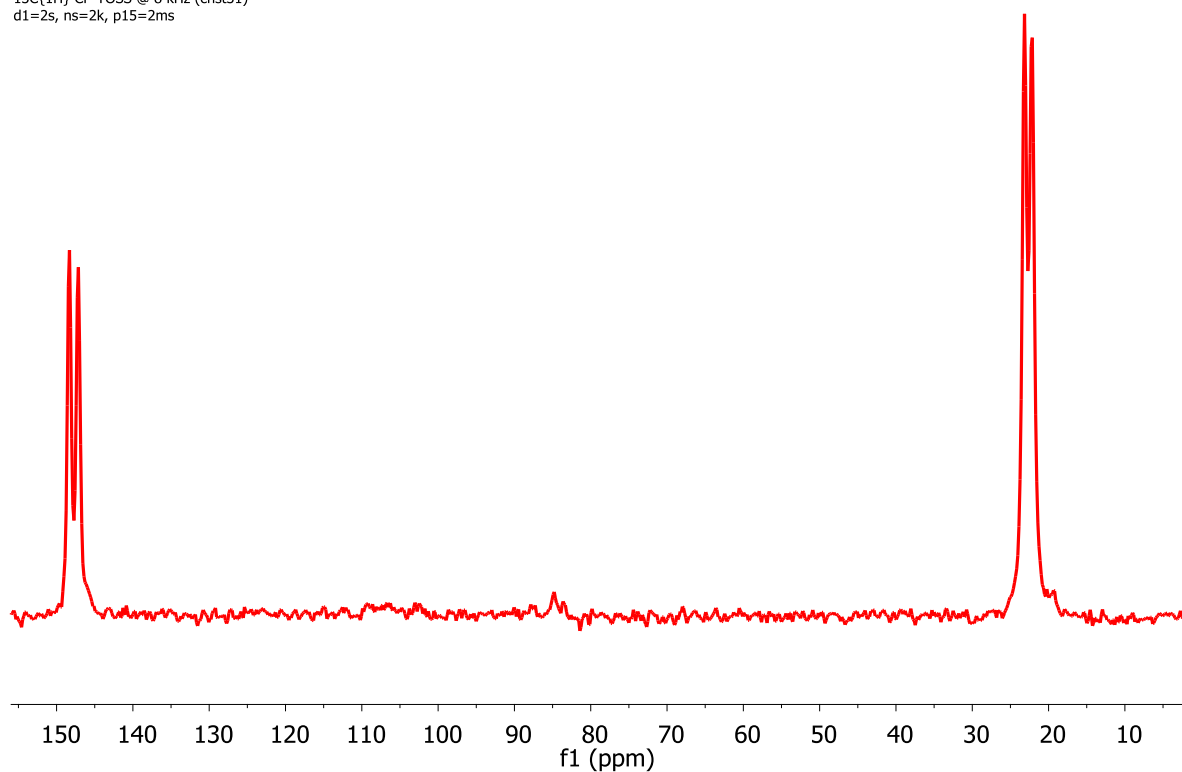


Figure S8. Solid-state ^{13}C -NMR spectrum for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})]$ **2**. Total sideband suppression (CP-TOSS) experiment.

Mar10-16
Rebecca Smith Sample Ref: RS Ag-MeOH
13C{1H} CPMAS @ 10 kHz
d1=2s, ns=2560, p15=1ms

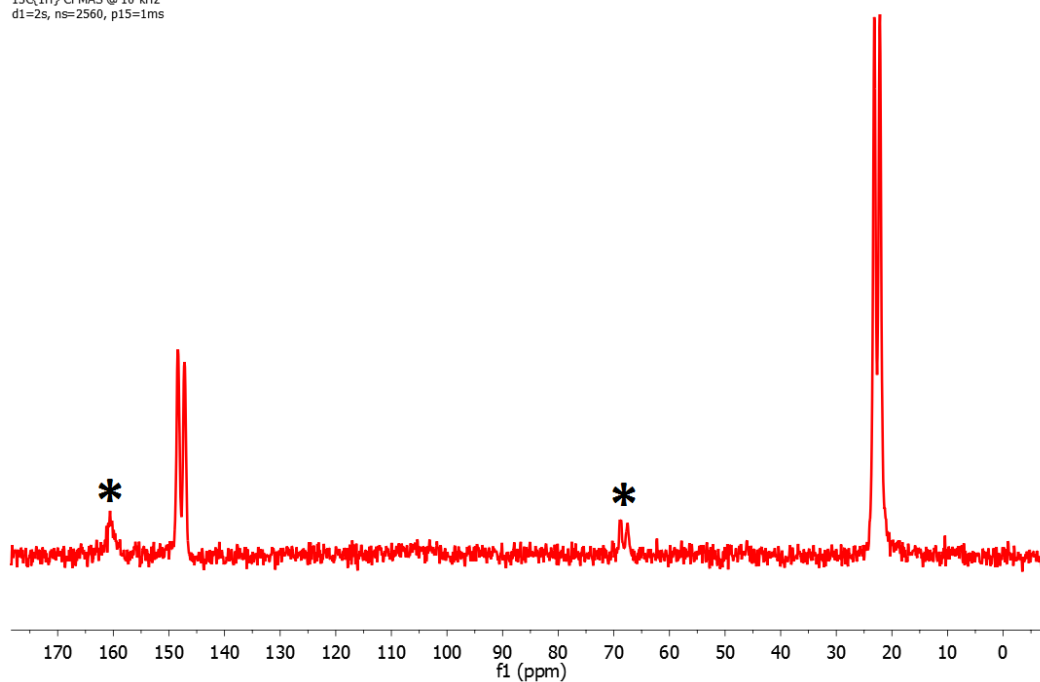


Figure S9. Attempt to collect solid-state ^{13}C -NMR spectrum for **1-MeOH** or **1**, avoiding significant MeOH loss. Spectrum indicates MeOH loss has led to collapse of **1** to give **2**. Asterisks indicate spinning side bands.

Nov27-C13
Rebecca Smith Sample Ref: RS200116
13C{1H} CPMAS @ 10 kHz
d1=2s, ns=4096, p15=1ms

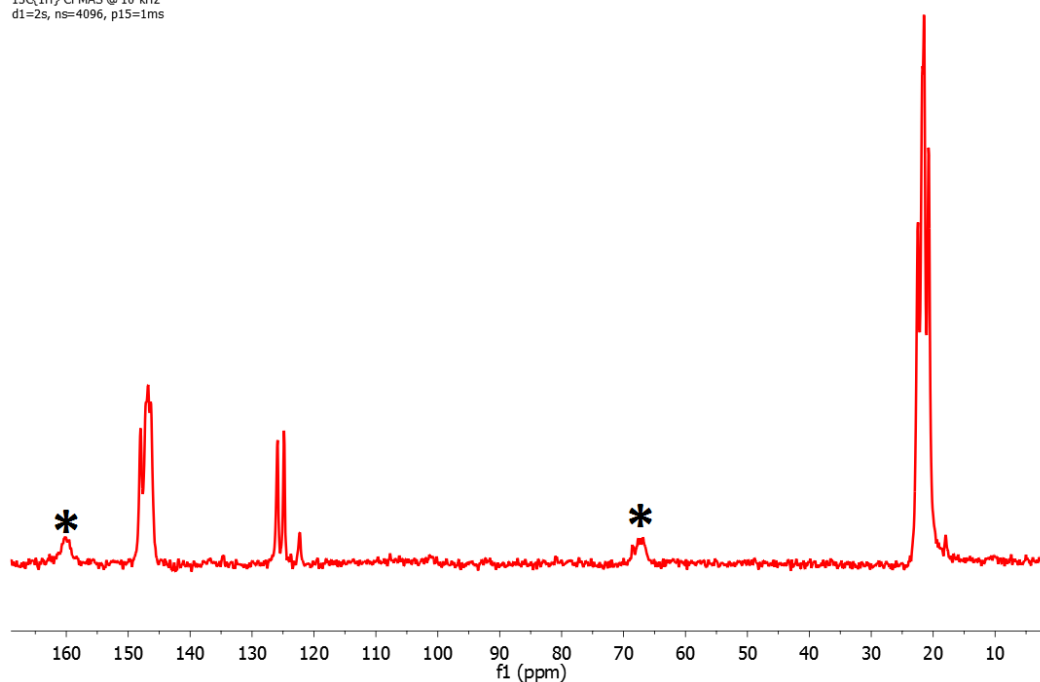


Figure S10. Solid-state ^{13}C -NMR spectrum for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{toluene})_x$. Asterisks indicate spinning side bands.

Ag p-xylene
Rebecca Smith Sample Ref: RS 070416 + p-xylene
13C{1H} CPMAS @ 10 kHz
d1=2s, ns=2560, p15=1ms

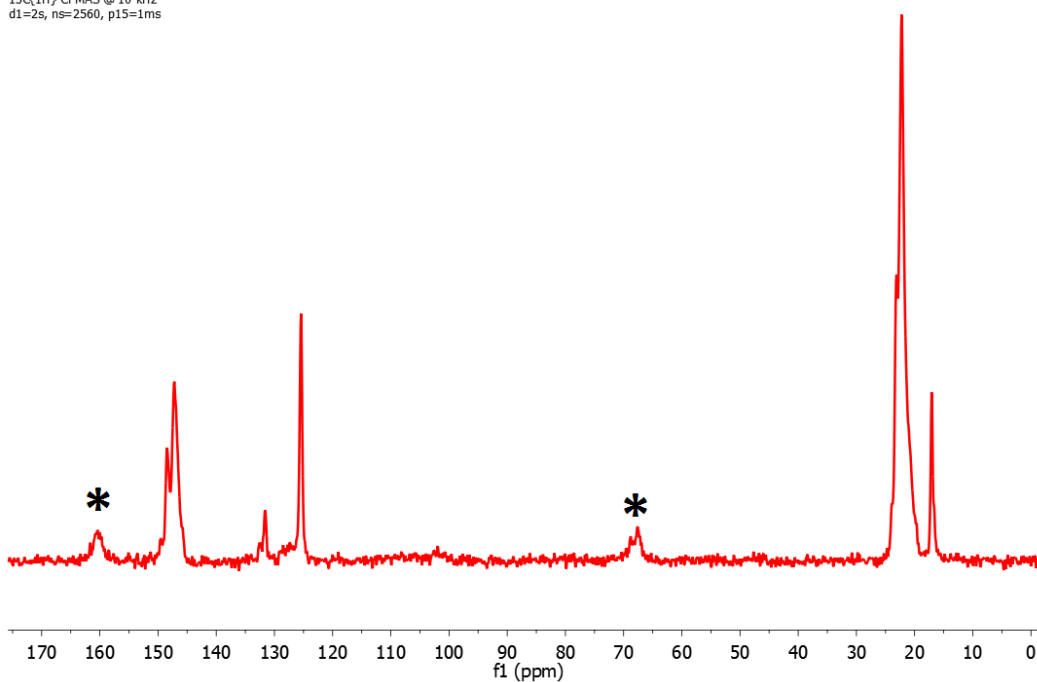


Figure S11. Solid-state ^{13}C -NMR spectrum for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (p\text{-xylene})_x$. Asterisks indicate spinning side bands.

Ag F4benzene
Rebecca Smith Sample Ref: Ag-F4-benzene
13C{1H} CPMAS @ 10 kHz
d1=2s, ns=512, p15=1ms

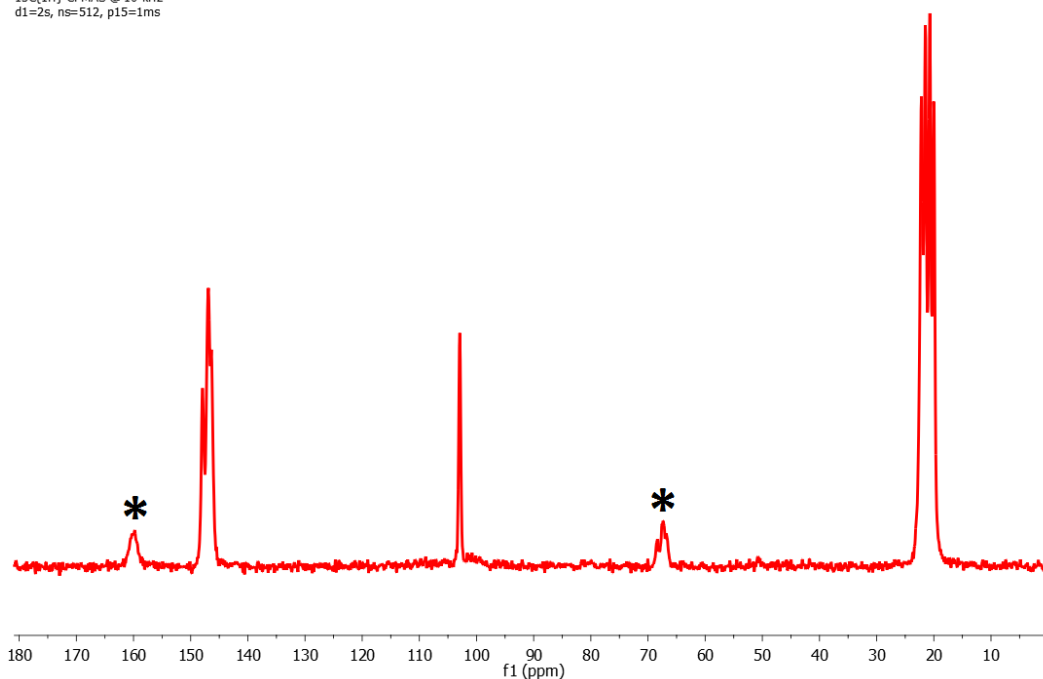


Figure S12. Solid-state ^{13}C -NMR spectrum for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (1,2,4,5\text{-tetrafluorobenzene})_x$. Asterisks indicate spinning side bands.

Ag tetramethylbenzene
Rebecca Smith Sample Ref: RS 070416 + tetramethylbenzene
13C[1H] CPMAS @ 10 kHz
d1=2s, ns=2560, p15=1ms

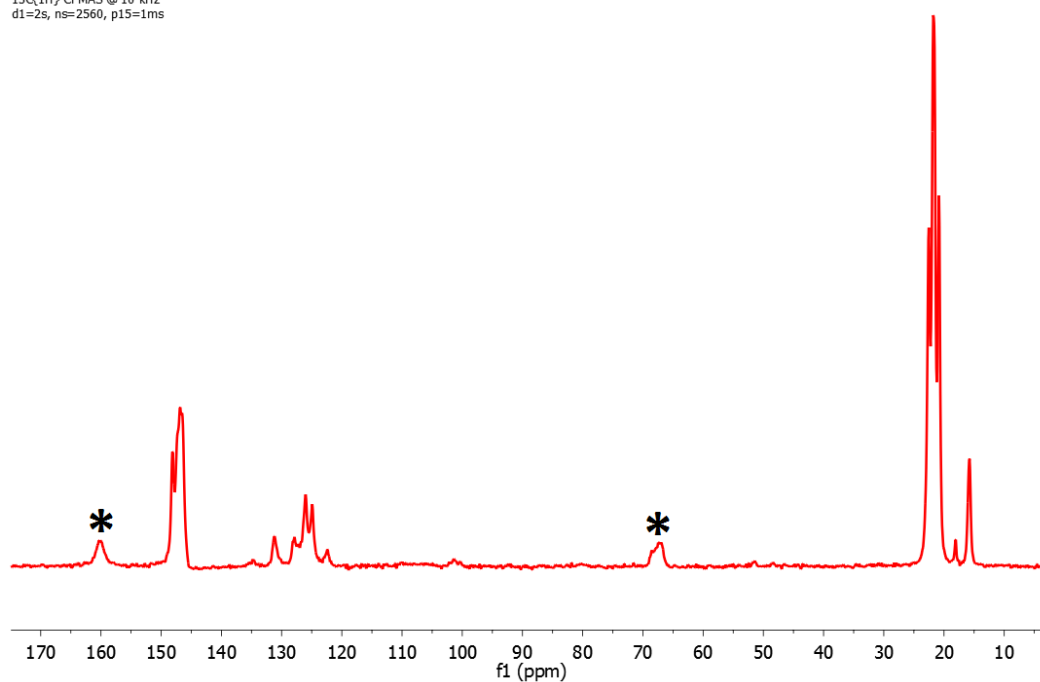


Figure S13. Solid-state ^{13}C -NMR spectrum for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})]\cdot(1,2,4,5\text{-tetramethylbenzene})_x$. Asterisks indicate spinning side bands.

5. ^1H NMR Spectroscopic Data

^1H spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer and. Guest-exchanged samples (~2-5 mg) of **1** were dissolved in DMSO- d_6 before analysis. Chemical shifts are reported in ppm relative to TMS (0 ppm) with the residual solvent resonances used as an internal reference. The NMR data were analysed using the Bruker Topspin programme suite. Guest concentrations were determined by comparing integrations of the guest and TMP signals.

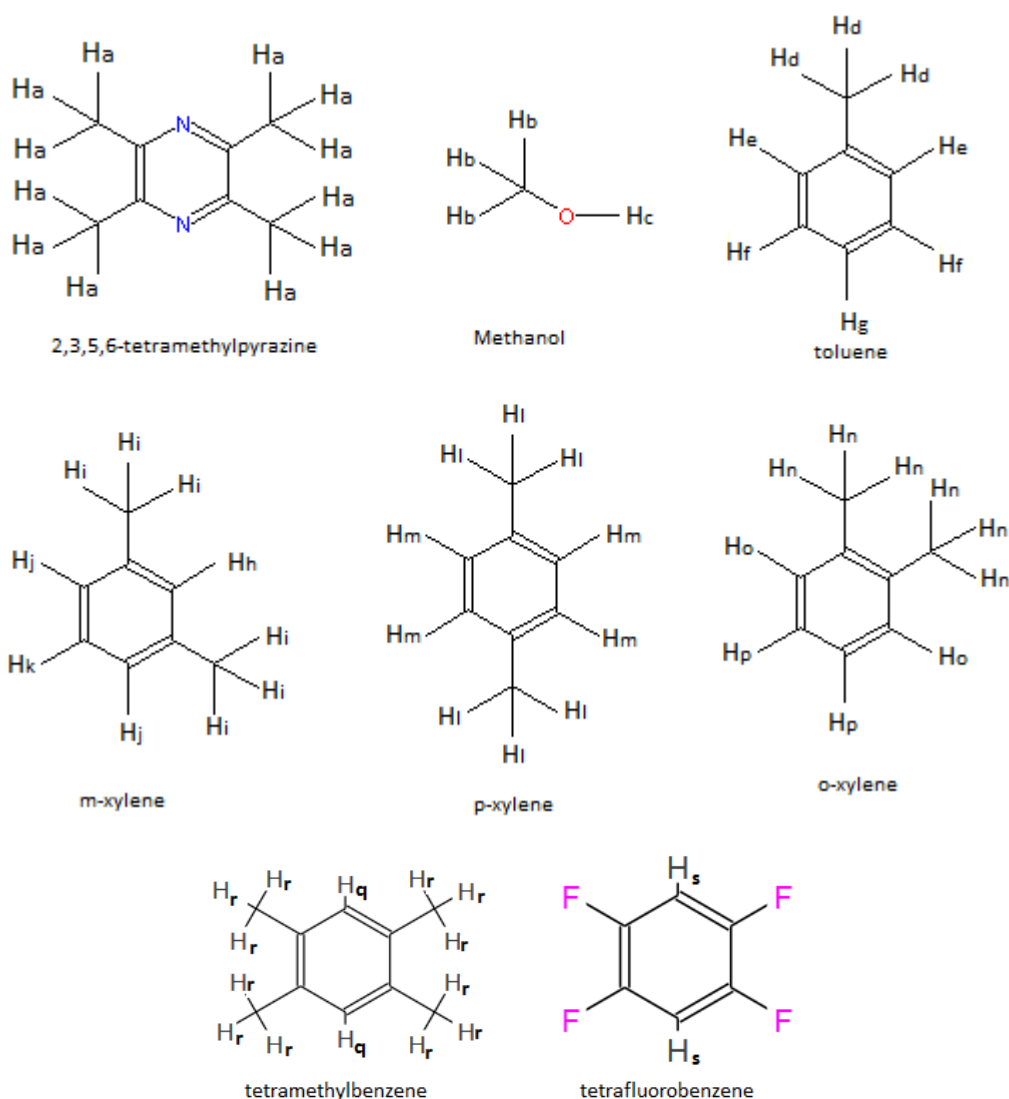


Figure S14. Proton environments for ^1H -NMR analytes in this study, H_a - H_p

Table S1. ^1H -NMR data for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})]$ (**1**) after dissolution in DMSO

δ/ppm	Multiplicity	Assignment
2.38	singlet	H_a
2.51	singlet	DMSO
3.34	singlet	H_2O

Table S2. ^1H -NMR data for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})]\cdot(\text{toluene})_x$ ($x=0.68$) after dissolution in DMSO.

δ/ppm	Multiplicity	Assignment	Integration
2.29	singlet	H_d	0.17

2.37	singlet	H _a	1
2.49	singlet	DMSO	-
3.36	singlet	H ₂ O	-
7.1-7.3	multiplet	H _e , H _f , H _g	0.27

Table S3. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(*m*-xylene)_x (x=0.16) after dissolution in DMSO.

δ/ppm	Multiplicity	Assignment	Integration
2.09	singlet	H _i	0.08
2.38	singlet	H _a	1
2.51	singlet	DMSO	-
3.35	singlet	H ₂ O	-
7.0-7.2	multiplet	H _n , H _j , H _k	0.05

Table S4. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(*p*-xylene)_x (x=0.22) after dissolution in DMSO.

δ/ppm	Multiplicity	Assignment	Integration
2.24	singlet	H _l	0.11
2.38	singlet	H _a	1
2.52	singlet	DMSO	-
3.34	singlet	H ₂ O	-
7.05	singlet	H _m	0.07

Table S5. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(*o*-xylene)_x (x=0.44) after dissolution in DMSO. This sample appears to contain some methanol, approximately 0.08 per formula unit.

δ/ppm	Multiplicity	Assignment	Integration
2.21	singlet	H _n	0.22
2.39	singlet	H _a	1
2.52	singlet	DMSO	-
3.15	quartet	H _c	0.01
3.37	singlet	H ₂ O	-
4.11	doublet	H _b	0.02
7-7.2	multiplet	H _o , H _p	0.14

Table S6. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(tetramethylbenzene)_x (x=0.16) after dissolution in DMSO

δ/ppm	Multiplicity	Assignment	Integration
2.21	singlet	H _r	0.16
2.38	singlet	H _a	1
2.51	singlet	DMSO	-
3.35	singlet	H ₂ O	-

7.03	singlet	H _q	0.02
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Table S7. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(cyclohexane)_x (x=0) after dissolution in DMSO

δ/ppm	Multiplicity	Assignment
2.38	singlet	H _a
2.51	singlet	DMSO
3.37	singlet	H ₂ O

Table S8. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(perfluoro(methylcyclohexane))_x after dissolution in DMSO. Impurity could arise from perfluoro(methylcyclohexane), which has a purity of 90% for the commercial material used.

δ/ppm	Multiplicity	Assignment
2.39	singlet	H _a
2.52	singlet	DMSO
3.18	doublet	impurity
3.34	singlet	H ₂ O

Table S9. ¹H-NMR data for [Ag₂(O₂CCF₂CF₂CO₂)(TMP)]·(tetrafluorobenzene)_x (x=0.24) after dissolution in DMSO.

δ/ppm	Multiplicity	Assignment	Integration
2.31	singlet	H _a	1
2.50	singlet	DMSO	-
3.26	singlet	H ₂ O	-
7.64	singlet	H _s	0.04

6. Gas Chromatographic Data

Samples of guest-soaked MOF (approx. 2-5 mg) were lightly dried in air for 5 min before dissolving in DMSO. The solutions were transferred to screw cap glass vials, and then analysed using a Perkin-Elmer Autosystem GC with an Alltech™ Heliflex™ AT-1 capillary column (L x I.D. 30 m x 0.32 mm x df 5.00 μm), heating from 40 to 200 °C at 10 °C min⁻¹. Expected guest retention times were determined from DMSO solutions of each guest and found to be 2.2 min (methanol), 3.6 min (perfluoro(methylcyclohexane)), 9.6 min (1,2,4,5-tetrafluorobenzene), 10.3 min (cyclohexane), 11.39 min (pentane), 12.8 min (toluene), 15.1 min (p-xylene), 15.2 min (m-xylene) and 15.6 min (o-xylene). Relative content of guests was determined by comparing peak areas to that of TMP (retention time 18.9 min).

Table S10. Summary of guest contents determined by GC

Guest	Guest/TMP ratio
toluene	1.60
<i>o</i> -xylene	1.97
<i>m</i> -xylene	0.85
<i>p</i> -xylene	0.38
tetrafluorobenzene	0.32
pentane	0.00
cyclohexane	0.01
perfluoro-(methylcyclohexane)	0.00

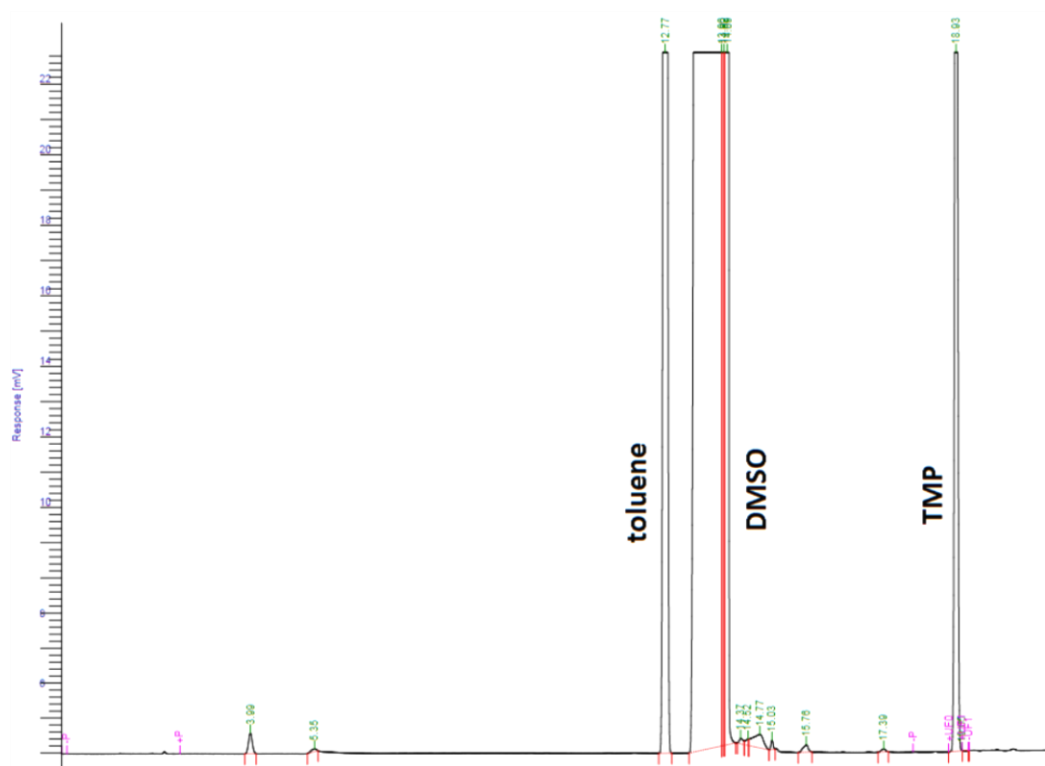


Figure S15. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{toluene})_x$ after dissolution in DMSO.

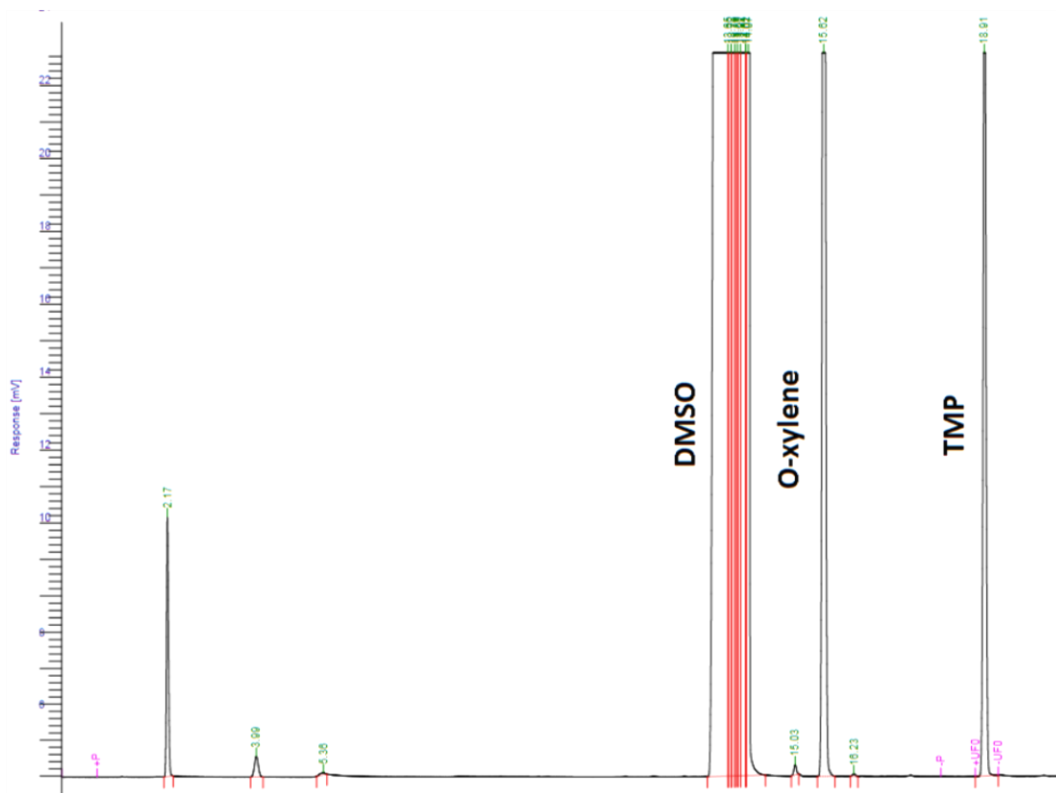


Figure S16. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (o\text{-xylene})_x$ after dissolution in DMSO.

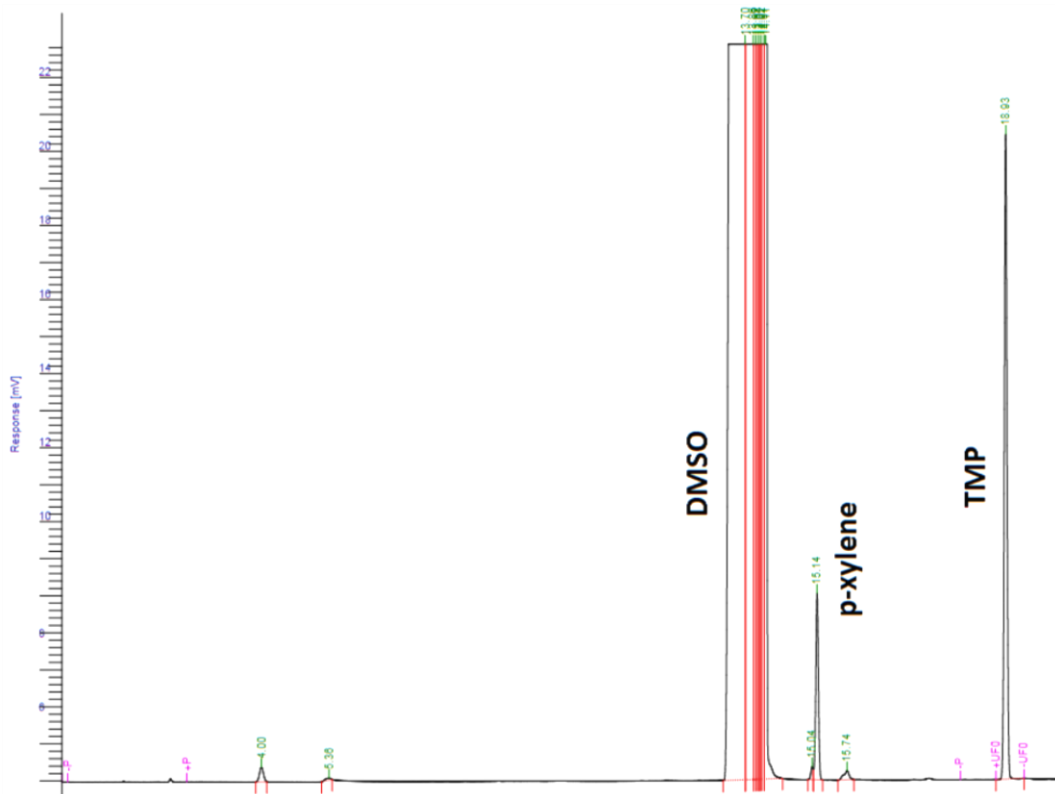


Figure S18. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{p-xylene})_x$ after dissolution in DMSO.

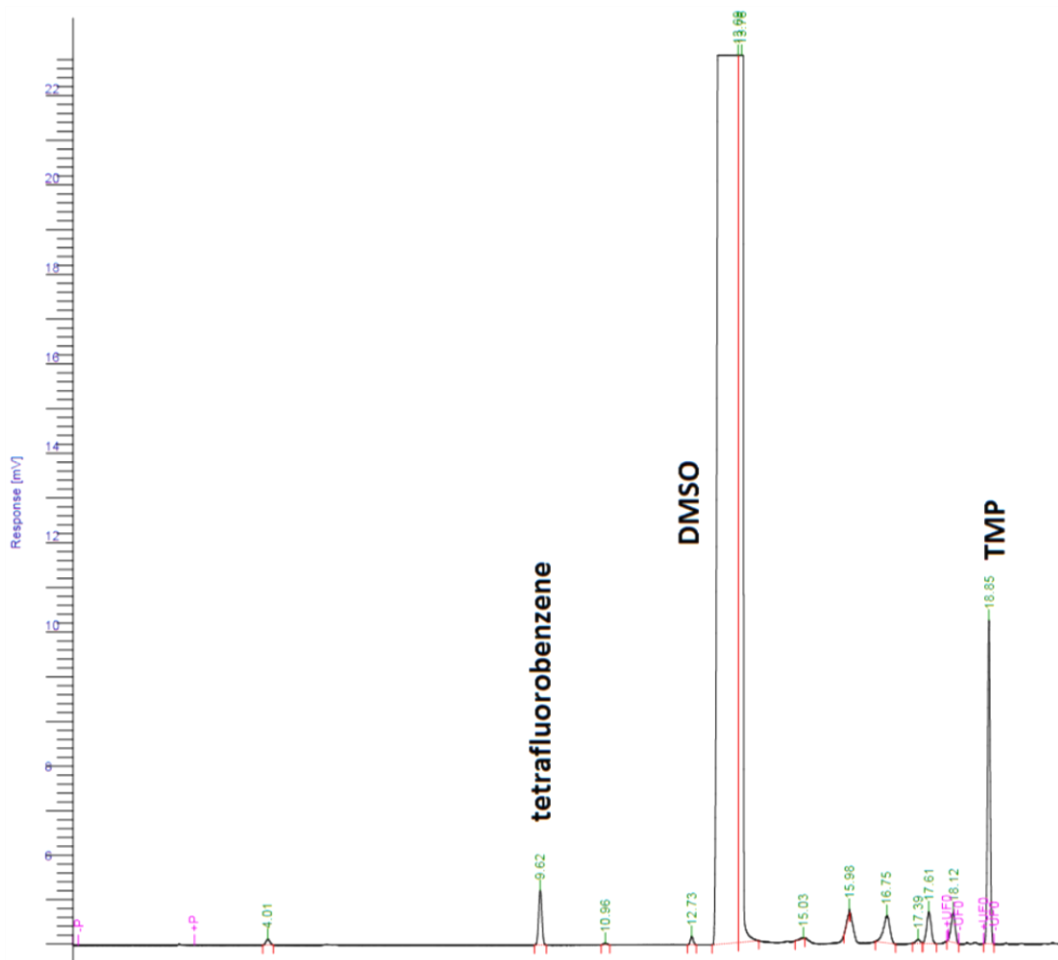


Figure S19. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{tetrafluorobenzene})_x$ after dissolution in DMSO.

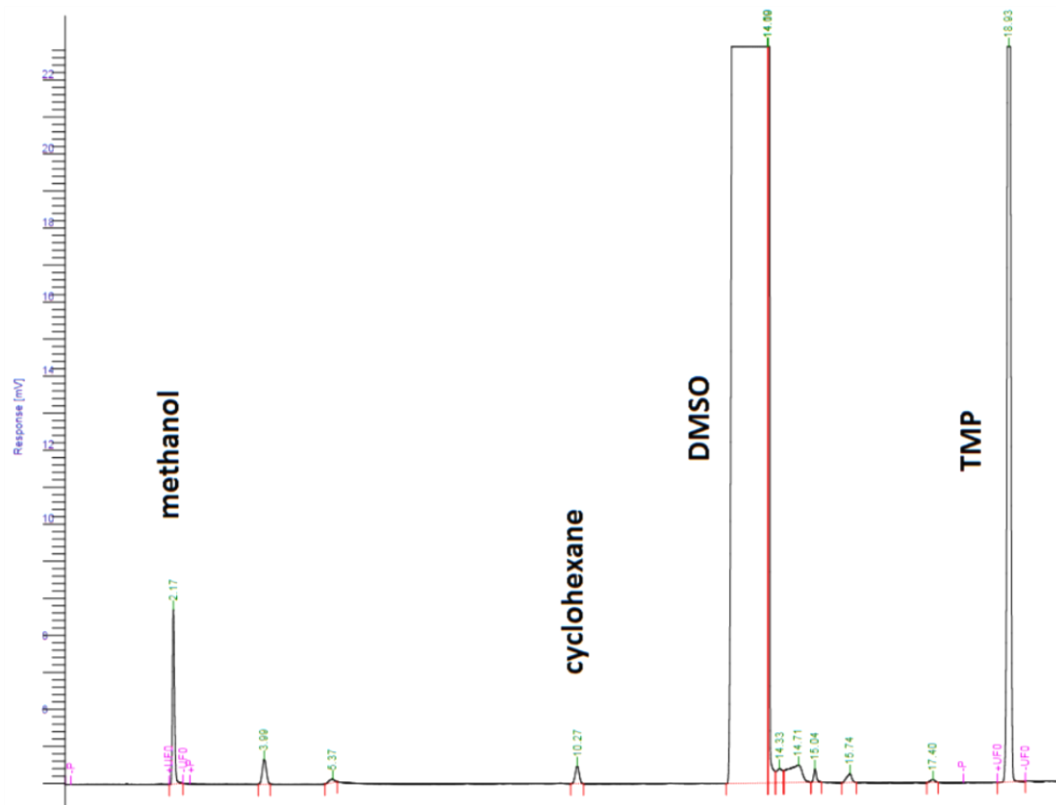


Figure S20. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{cyclohexane})_x$ after dissolution in DMSO.

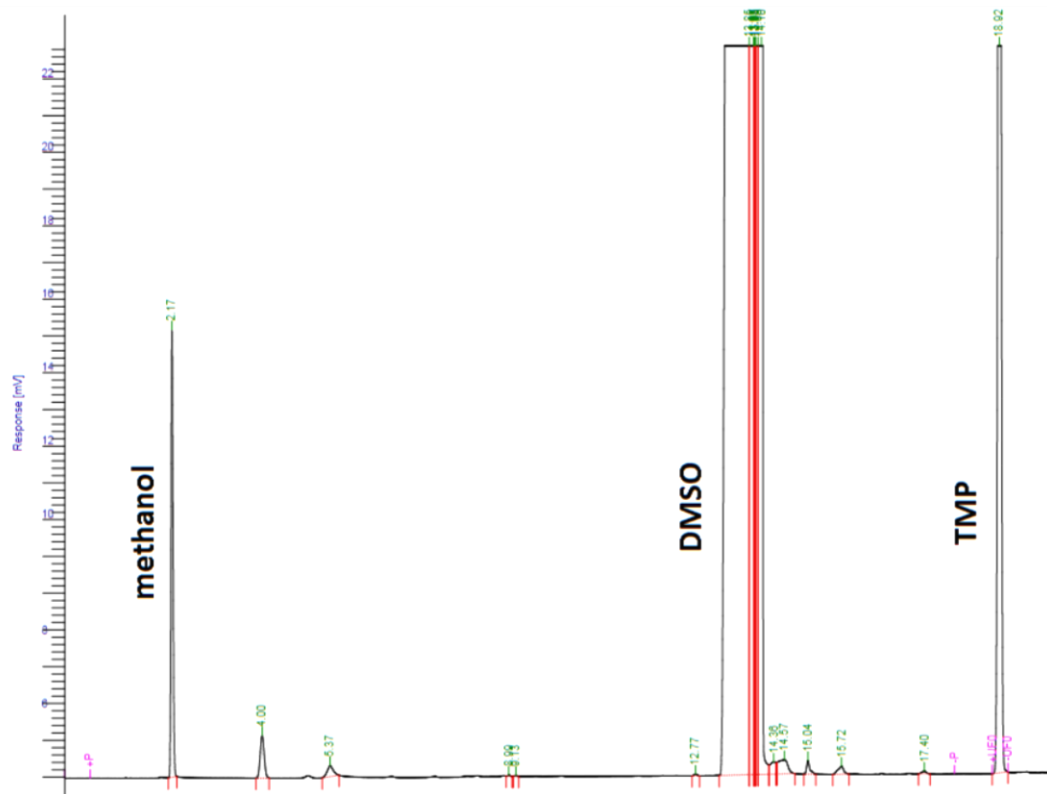


Figure S21. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})] \cdot (\text{pentane})_x$ after dissolution in DMSO.

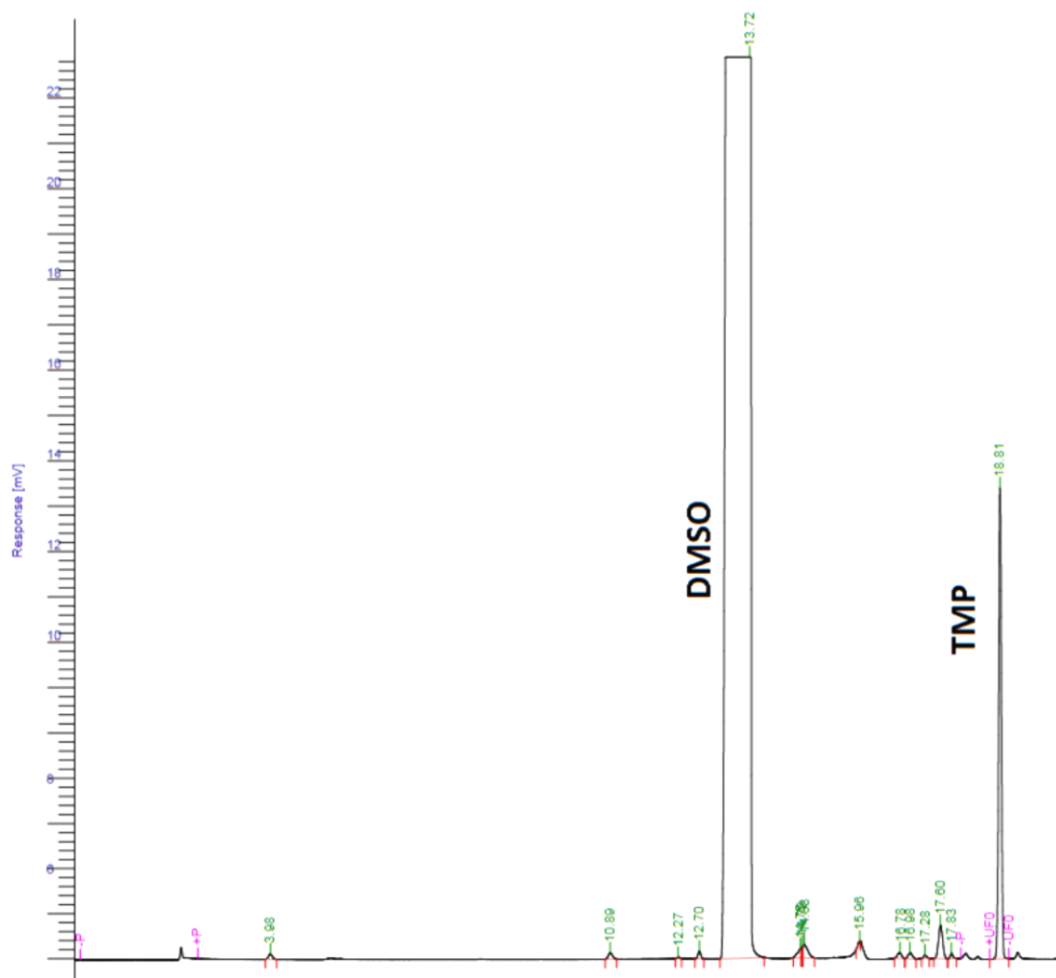


Figure S22. Gas chromatogram for $[\text{Ag}_2(\text{O}_2\text{CCF}_2\text{CF}_2\text{CO}_2)(\text{TMP})](\text{perfluoro(methylcyclohexane)})_x$ after dissolution in DMSO.