Supporting Information

Synthesis and crystal structure of a [2+4]-type organic cage based on calix[4]arene

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Fig. S14. PLATON CAVITY illustration of the structure of the COC. The orange spheres, with a contact radius of at least 1.2 Å, represent the infinite solvent-accessible voids in this structure.

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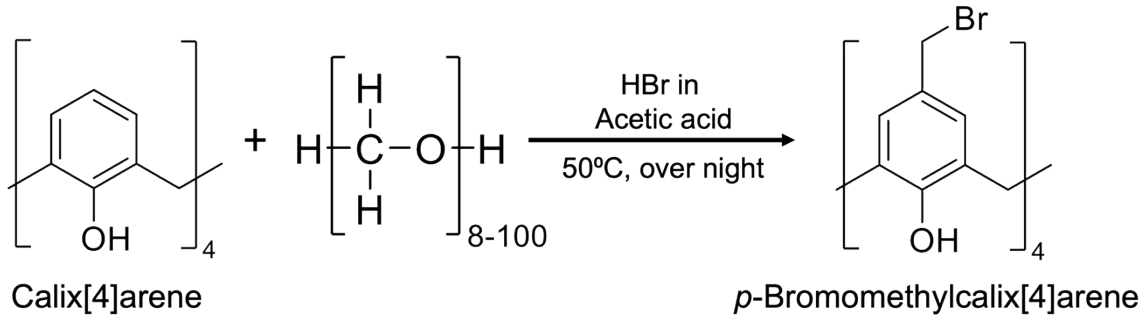
3. References

1. Experimental Section

Materials

Synthesis of *p*-bromomethylcalix[4]arene

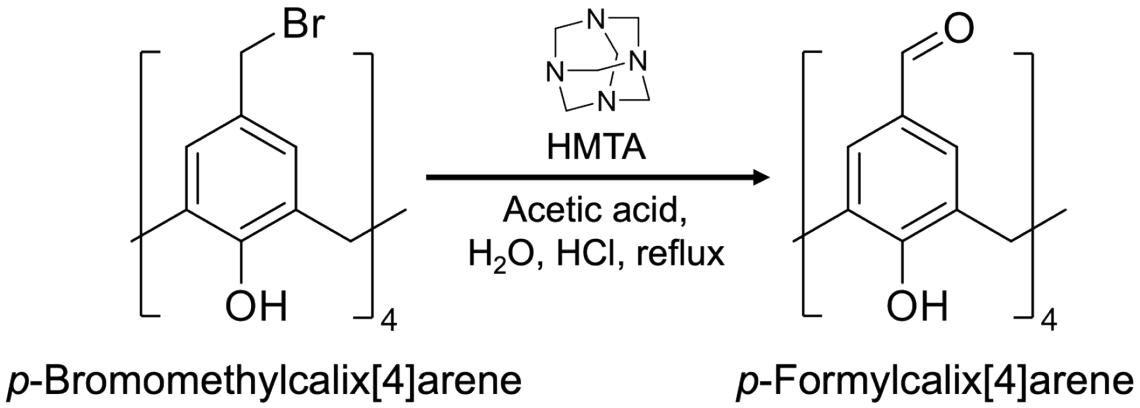


Scheme S1. Synthesis of *p*-bromomethylcalix[4]arene.

p-Bromomethylcalix[4]arene was synthesized by a procedure based on previous literature.[S1] Calix[4]arene (7.00 g, 16.5 mmol) and paraformaldehyde (4.00 g, 133.2 mmol) were dispersed in HBr (100 g, 30% v/v in acetic acid). The reaction was heated to 50 °C overnight, and after cooling to RT, the suspension was poured onto iced water (240 mL) and stirred for 30 min. The pink product was filtered, washed with water (2 × 400 mL), and dried. The yield of *p*-bromomethylcalix[4]arene was approximately 97.4% (12.8 g).

^{1}H NMR (500 MHz, 25 °C, $CDCl_3$-d_1): δ = 10.10 (s, 4H, O*H*), 7.06 (s, 8H, Ar*H*), 4.32 (s, 8H, CH_2Br), 4.11 (bs, 4H, ArCH_2Ar), 3.59 (bs, 4H, ArCH_2Ar). ^{13}C NMR (500 MHz, 25 ℃, $CDCl_3$-d_1): δ = 31.56 (*Ar–CH$_2$–Ar*), 33.29 (*Ar–CH$_2$–Br*), 128.26 (*Ar–CH*), 129.94 (*Ar–CH*), 131.69 (*Ar–CH*), 148.91 (*Ar–O*).

Synthesis of *p*-formylcalix[4]arene

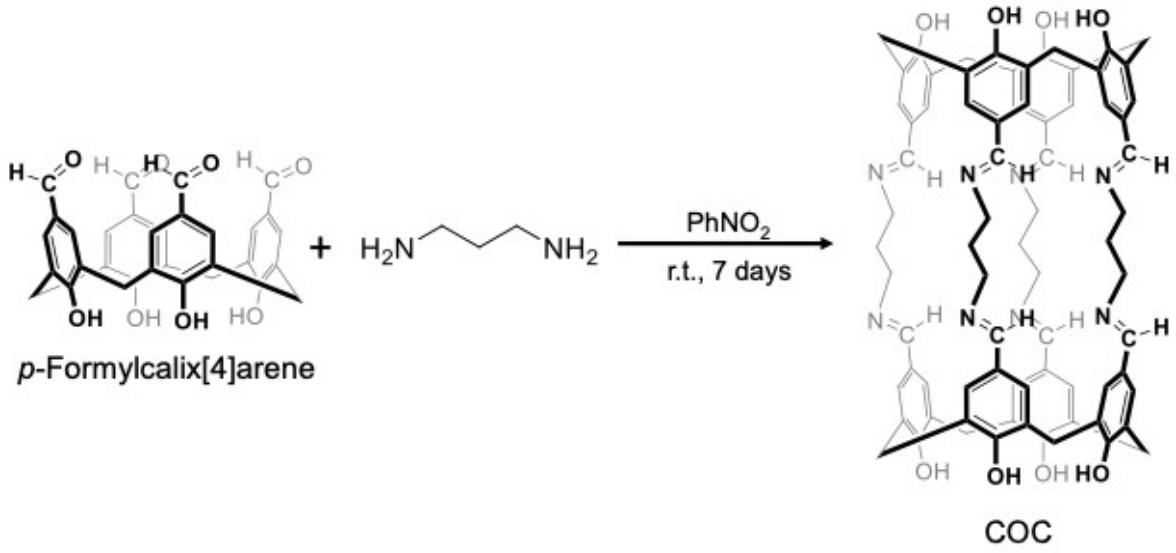


Scheme S2. Synthesis of *p*-formylcalix[4]arene.

p-Formylcalix[4]arene was synthesized by a procedure based on previous literature.[S1] *p*-Bromomethylcalix[4]arene (10.02 g, 12.58 mmol) and HMTA (14.12 g, 100.8 mmol) were suspended in glacial acetic acid (66 mL) and were stirred for 30 min at room temperature. Water (66 mL) was added, and stirred for 30 min at ambient temperature, then refluxed for 2 h. Conc. HCl (16 mL) was added and refluxed for a further 2 h. Then the mixture was cooled to room temperature, and the yellow precipitated was filtered, washed with water (2 × 400 mL) and then ethanol (60 mL) and dried. The yield of *p*-formylcalix[4]arene was approximately 91.1% (6.16 g).

^{1}H NMR (500 MHz, 25 °C, DMSO-d_6): δ = 9.76 (s, 4H, O*H*), 7.65 (s, 8H, Ar*H*). ^{13}C NMR (500 MHz, 25 ℃, DMSO-d_6): δ = 31.09 (*Ar–CH$_2$–Ar*), 127.90 (*Ar–CH*), 129.77 (*Ar–CH*), 130.51 (*Ar–CH*), 160.33 (*Ar–O*), 190.46 (*Ar–CHO*).

Synthesis of the [2+4]-type calixarene-based organic cage (COC)



Scheme S3. Synthesis of the COC.

p-Formylcalix[4]arene (1.100 g, 2.05 mmol) was dissolved in nitrobenzene (240 mL). 1,3-Propanediamine (0.300 g, 4.05 mmol) was then added and allowed to stand at room temperature for 7 d. The precipitated solid was filtered by suction and washed well with methanol. It was vacuum-dried at 40 °C to obtain a yellow solid. The yield of the COC was approximately 90.5% (1.137 g).

^{1}H NMR (500 MHz, 25 °C, DMSO-d_6): δ = 8.03 (s, 8H, NC*H*), 7.38 (s, 16H, Ar*H*), 4.22 (bs, 8H, ArCH_2Ar), 3.51 (bs, 8H, ArCH_2Ar), 1.65 (m, 8H, NCH$_2$CH_2CH$_2$N). FT-ICR MS: $[M+H]^+$ calcd. for COC ($C_{76}H_{72}N_8O_8$) 1225.55459; found 1225.55490. Elemental analysis for COC·2.2 DMSO (The sample was prepared by crystallization from DMSO and 1-PrOH, followed by drying in vacuo at 120 °C for 24 h): Calcd for $C_{80.4}H_{85.2}N_8O_{10.2}S_{2.2}$: C 69.10, H 6.15, N 8.02%; Found: C 69.13, H 6.32, N 8.24%.

Methods

Crystallographic Data

Table S1. Crystallographic data and structure refinement for the COC.

	The COC
Crystallization Solvent	DMSO/1-PrOH
Collection Temperature (K)	150
Formula	$C_{76}H_{72}N_8O_8$
Formula Weight	1225.416
Crystal system	triclinic
Space group	*P*-1
a [Å]	10.5410(4)
b [Å]	15.7908(5)
c [Å]	16.3627(7)
α [°]	108.584(3)
β [°]	102.988(3)
γ [°]	105.227(3)
V [Å^3]	2345.00(16)
Z	1
D_{calcd} [g cm^{-1}]	0.868
F(000)	648.0
θ_{max} [°]	25.249
Reflections collected /	36599 / 8489
unique	[R_{int} = 0.0572]
Data / restraints / parameter	8489 / 0 / 421
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.1078
	wR2 = 0.2890
R indices (all data)	*R1* = 0.1539
	wR2 = 0.3154
Good-of-fit on F^2	1.128
Largest different peak and hole [e.A^{-3}]	0.482 and -0.300
CCDC	2450199

2. Supporting figures

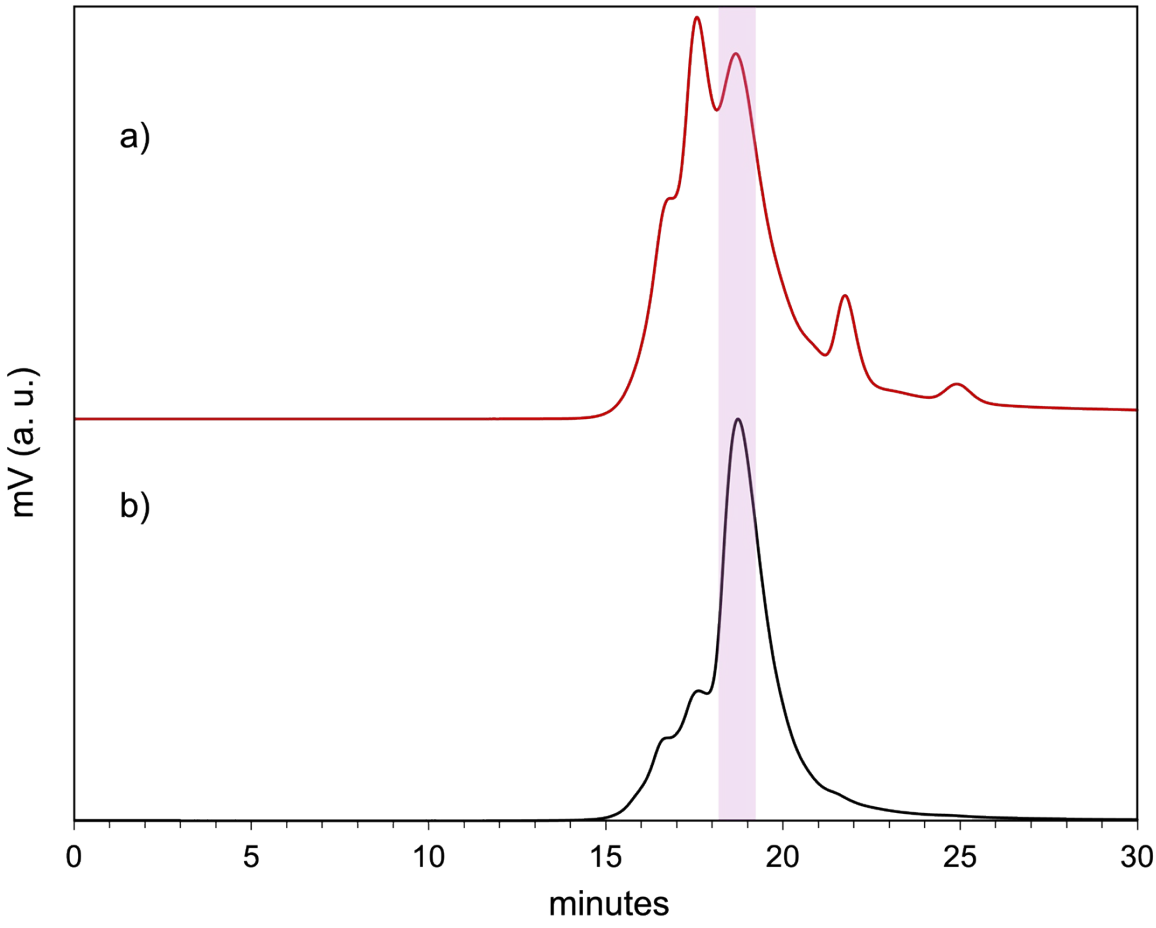


Fig. S1. Comparison of GPC curves after synthesis of the COC at different concentrations of *p*-formylcalix[4]arene, a) 0.02 mol/L (red line) and b) 0.01 mol/L (black line).

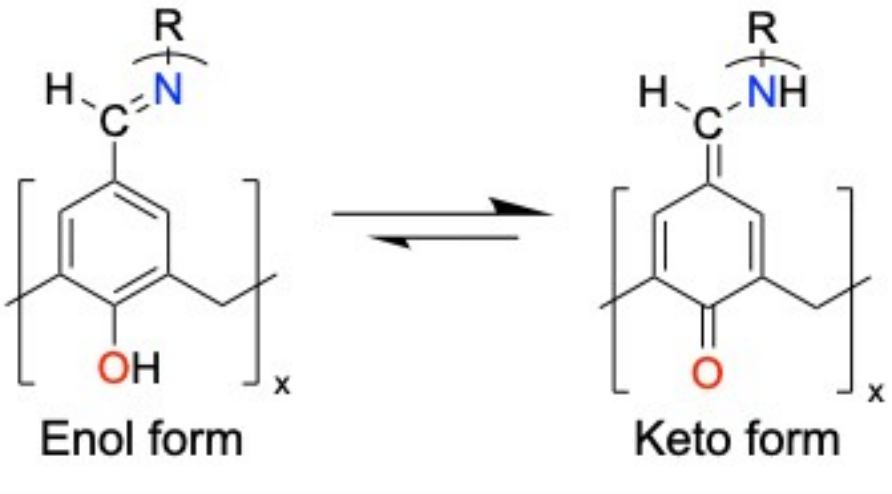


Fig. S2. Keto-enol tautomerization in the COC.

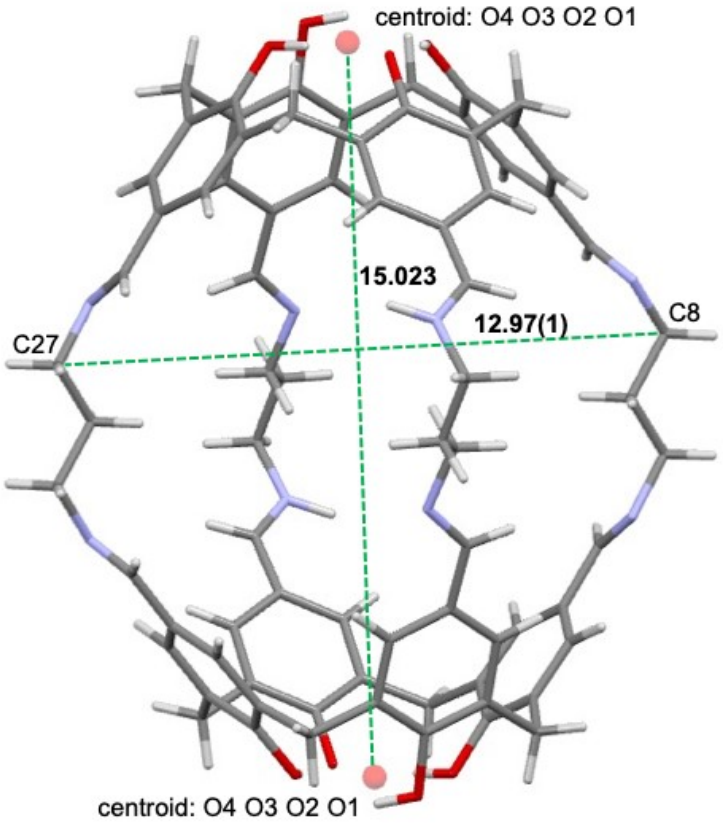


Fig. S3. Measured dimensions of the COC molecule (View from [100] side).

The horizontal length was measured between the most distant carbon atoms (C8–C27), and the vertical length was measured between the centroids of the four oxygen atoms (O1, O2, O3, O4) in the calix[4]arene site. van der Waals radii are not considered when the cage dimensions are determined.

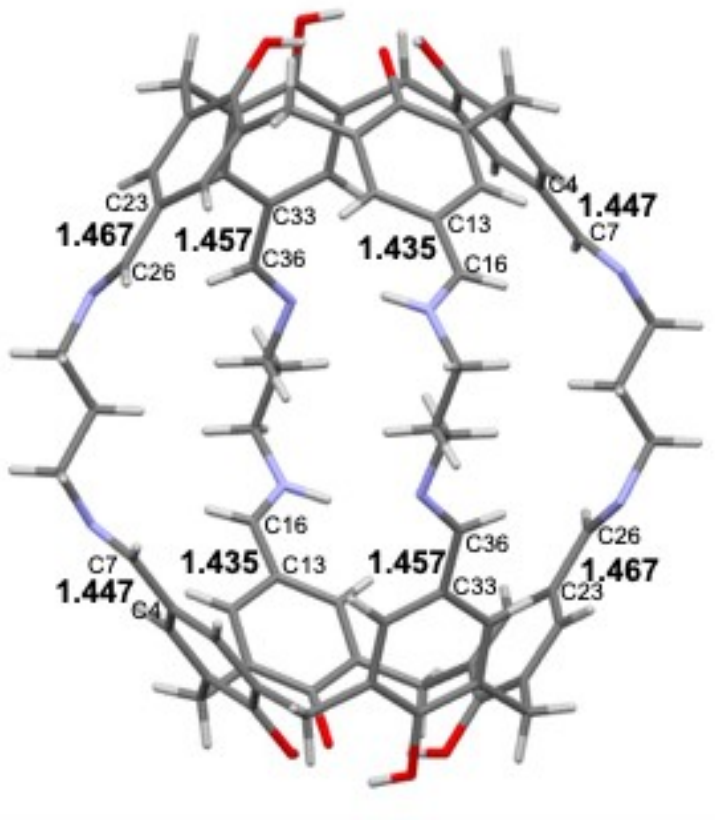


Fig. S4. C–C bond distances in the COC molecule (View from [100] side).

Table S2. List of interatomic distances related to Fig. S4.

Atoms	Distance(Å)
C4–C7	1.447(8)
C13–C16	1.435(7)
C23–C26	1.467(1)
C33–C36	1.457(7)

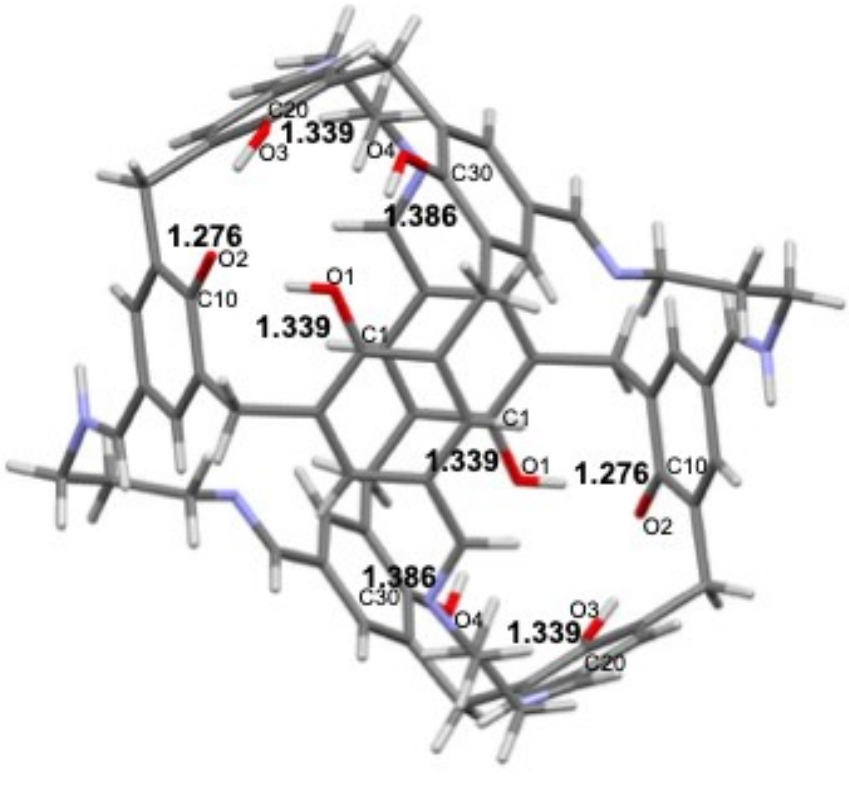


Fig. S5. C–O bond distances in the COC molecule (View from [001] side).

The typical length of phenolic C–O and C=O bonds are approximately 1.36 Å and 1.21 Å, respectively. Thus, the observed bond length between C10 and O2 in the COC was 1.276(7) Å, which can be determined to be a C=O bond.

Table S3. List of interatomic distances related to Fig. S5.

Atoms	Distance(Å)
O1–C1	1.339(6)
O2–C10	1.276(7)
O3–C20	1.339(9)
O4–C30	1.386(7)

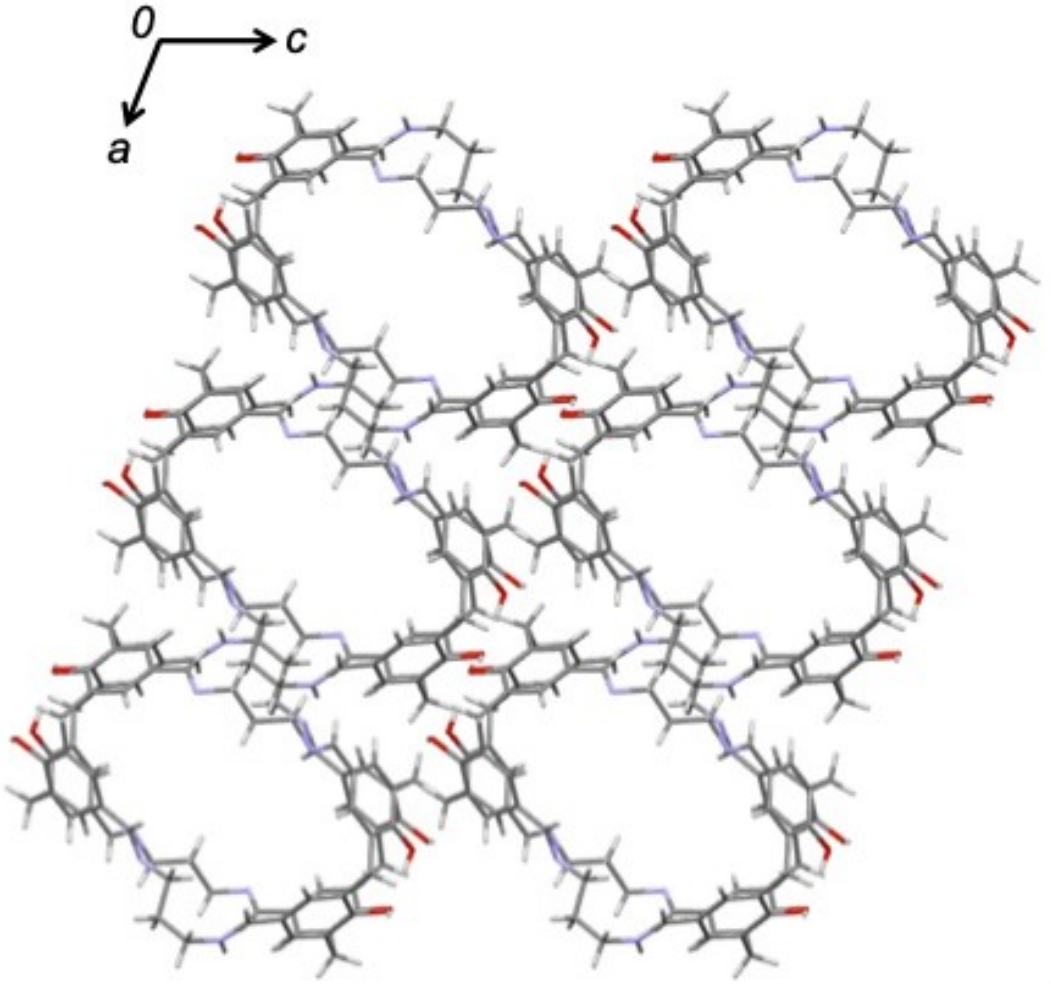


Fig. S6. Extended structure of the cage-like crystalline COC viewed from the [010] direction. The molecules are clearly packed into one-dimensional channels are formed along the a-axis through N-H···N hydrogen bonding and C-H···N interactions.

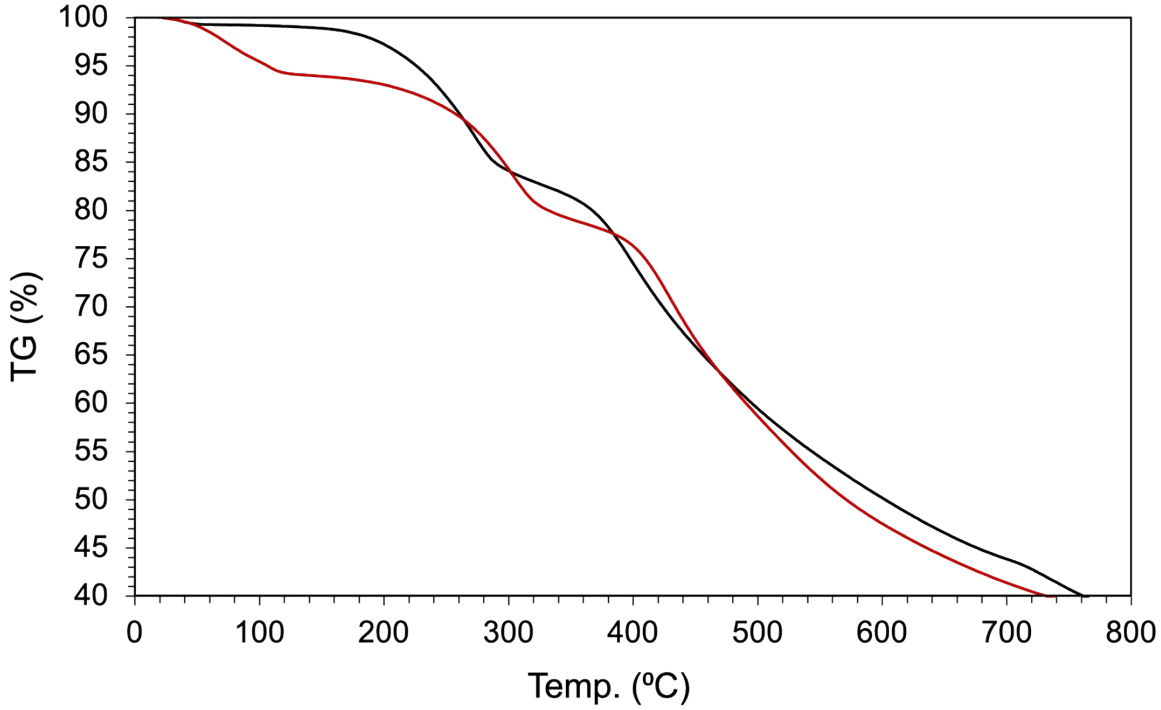


Fig. S7. TG curves comparison of the COC before (red line) and after (black line) the pretreatment process.

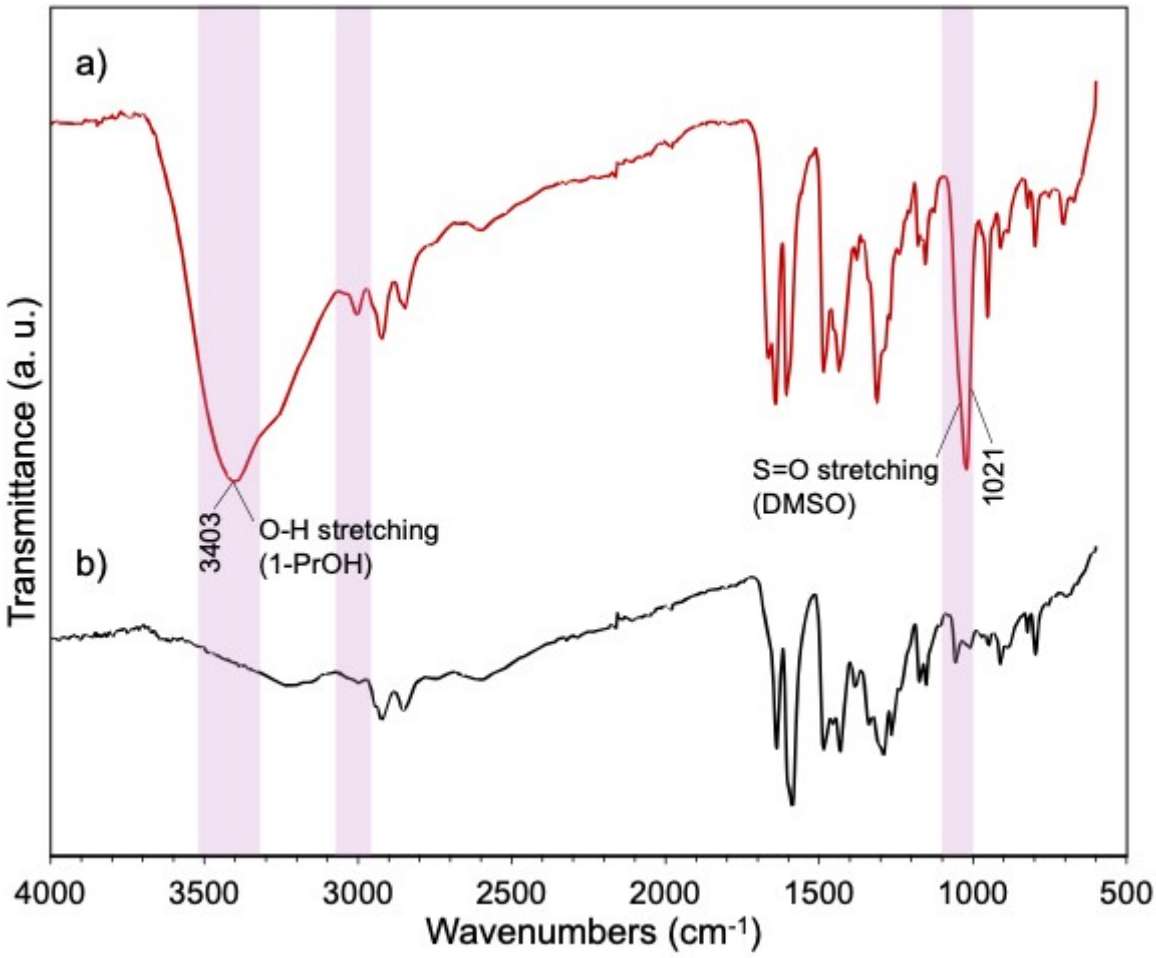


Fig. S8. FT-IR spectra of the COC a) before (red line) and b) after (black line) the pretreatment process.

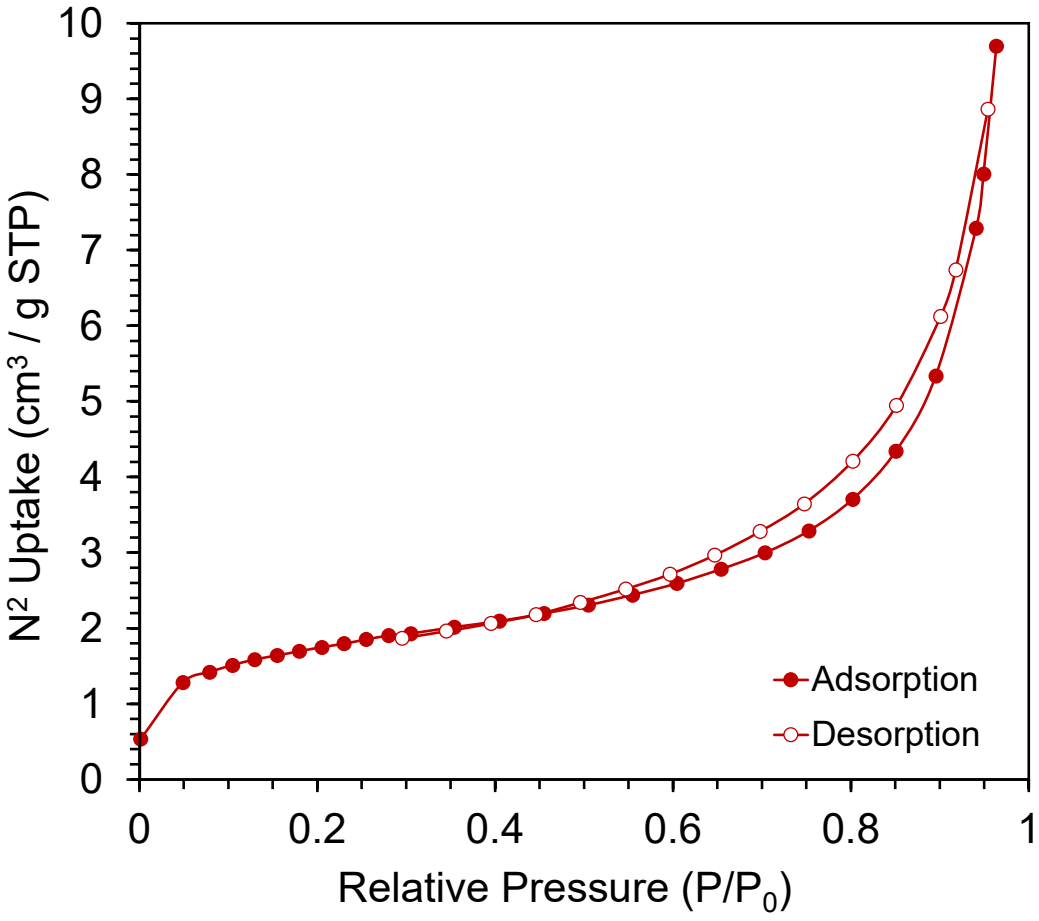


Fig. S9. N_2 adsorption–desorption isotherms of the activated COC crystals at 77 K. Solid circles: sorption; open circles: desorption.

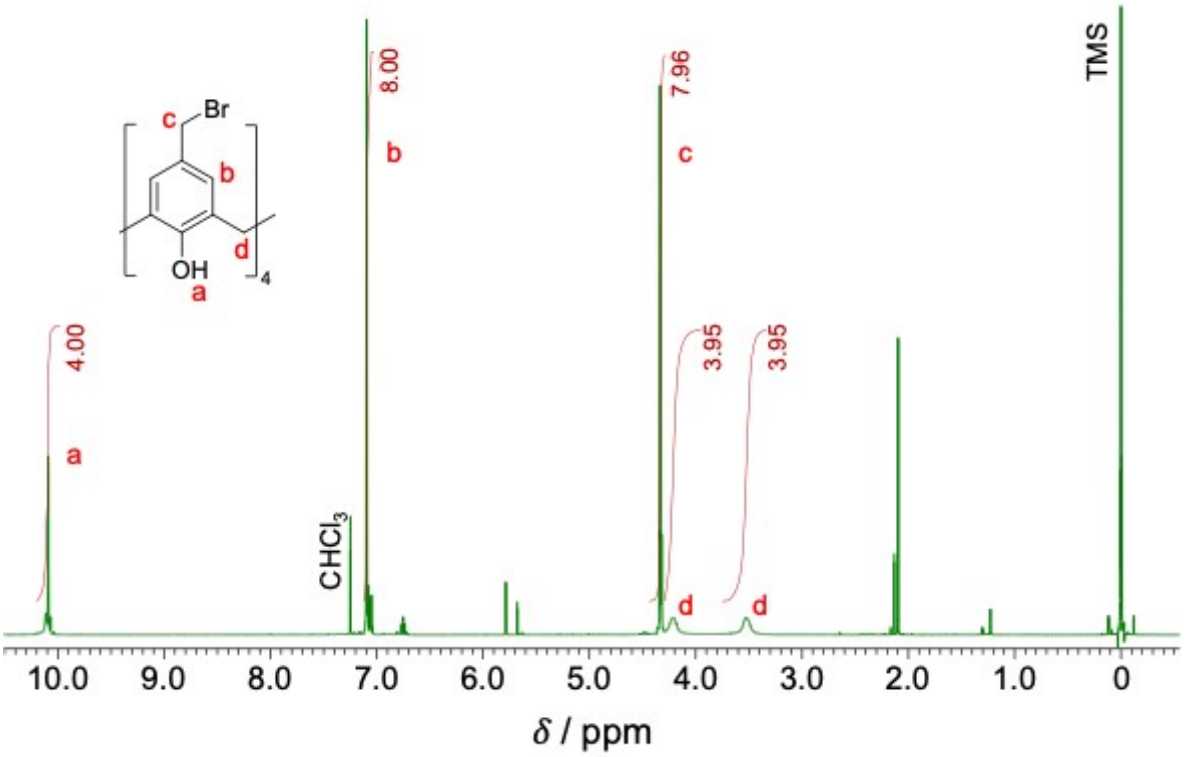


Fig. S10. 500 MHz ^{1}H NMR of the *p*-bromomethylcalix[4]arene (δ from TMS; $CDCl_3$-d_1, 298K).

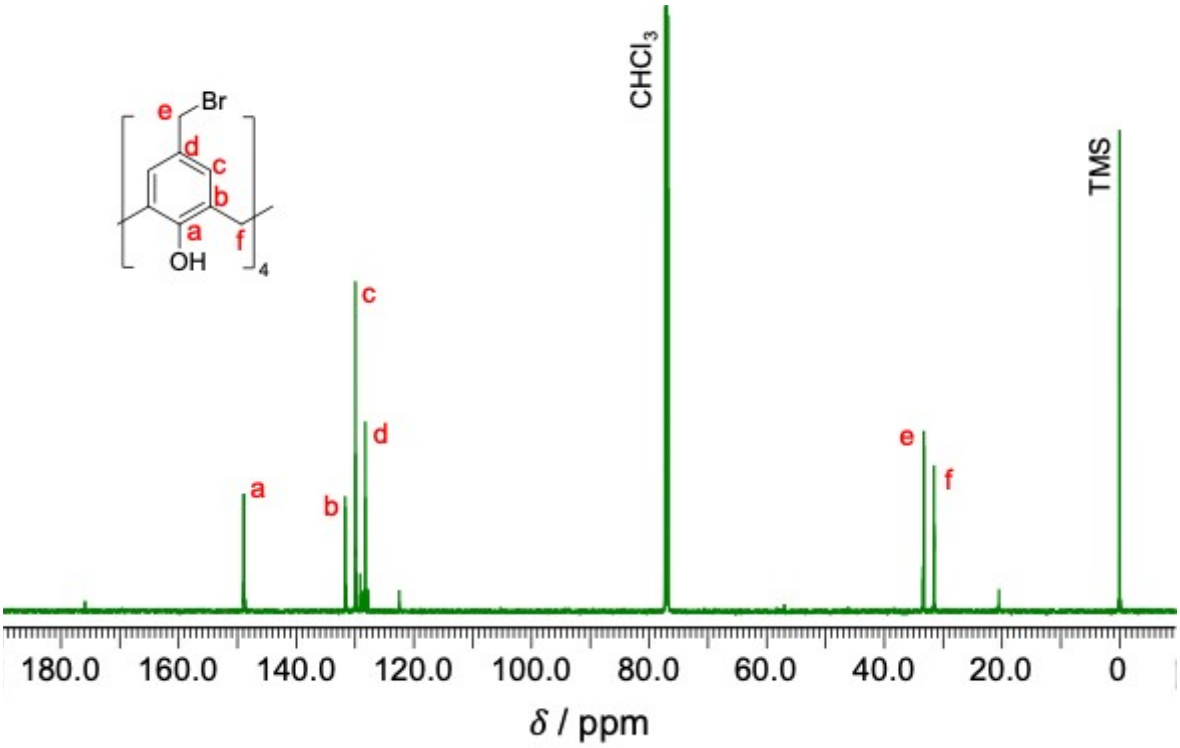


Fig. S11. 500 MHz ^{13}C NMR of the *p*-bromomethylcalix[4]arene (δ from TMS; $CDCl_3$-d_1, 298K).

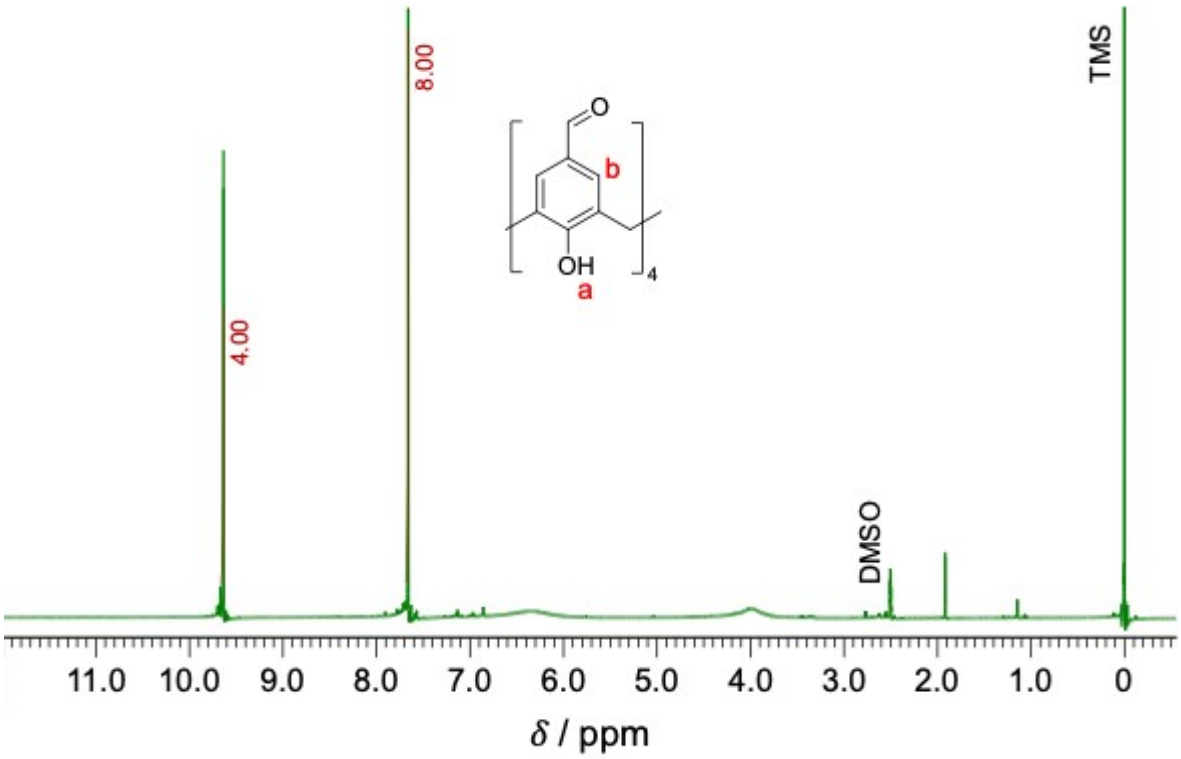


Fig. S12. 500 MHz ^{1}H NMR of the *p*-formylcalix[4]arene (δ from TMS; DMSO-d_6, 298K).

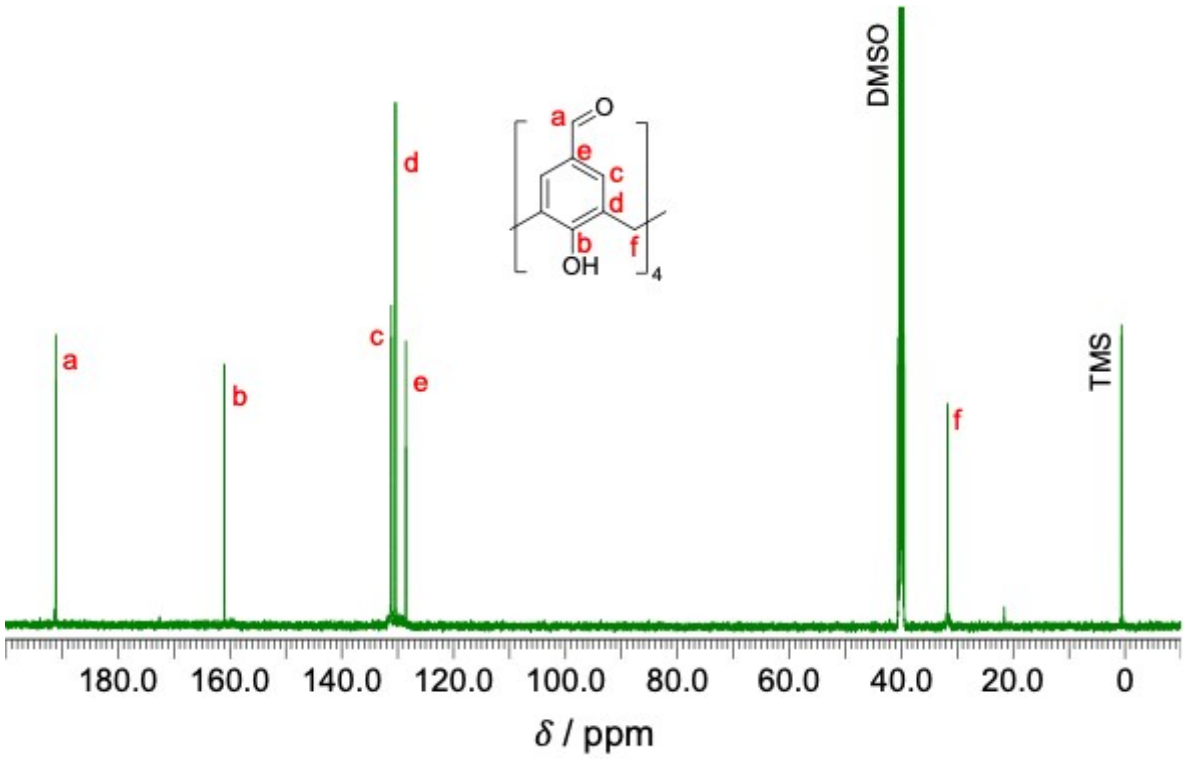


Fig. S13. 500 MHz ^{13}C NMR of the *p*-formylcalix[4]arene (δ from TMS; DMSO-d_6, 298K).

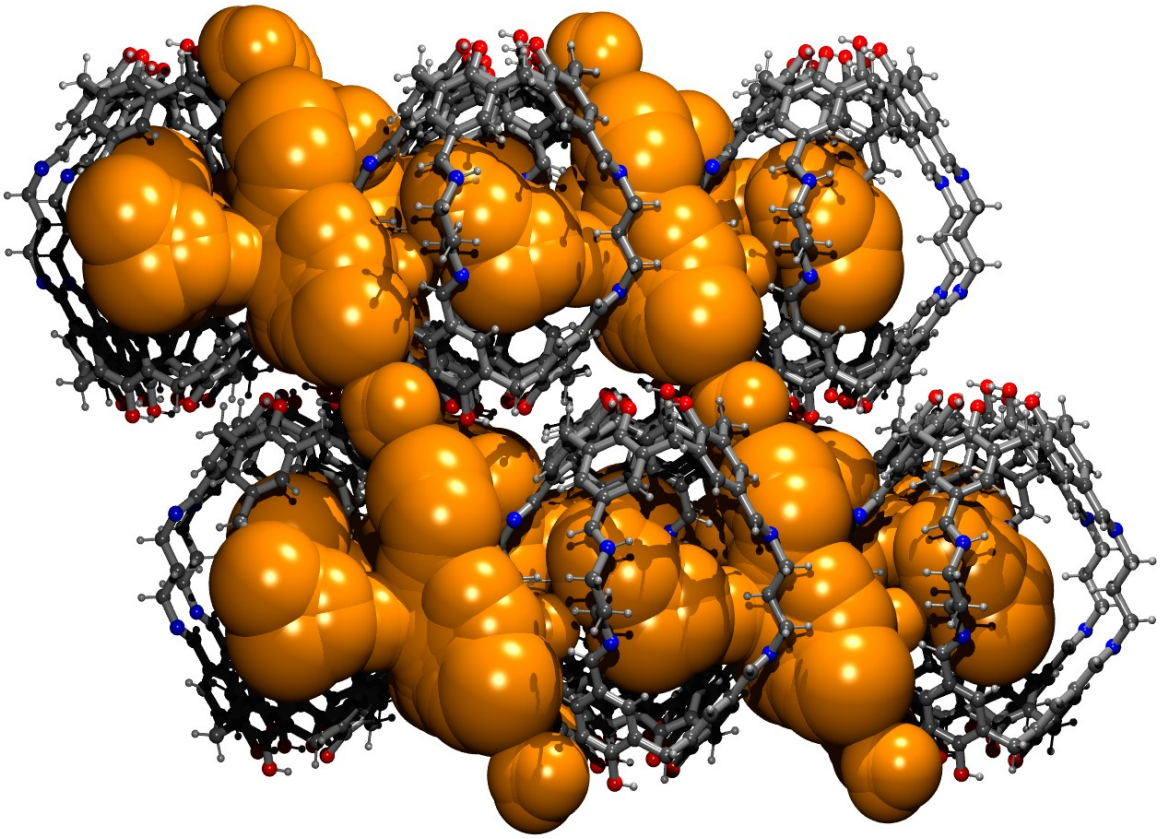


Fig. S14. PLATON CAVITY illustration[S2] of the structure of the COC. The orange spheres, with a contact radius of at least 1.2 Å, represent the infinite solvent-accessible voids in this structure.

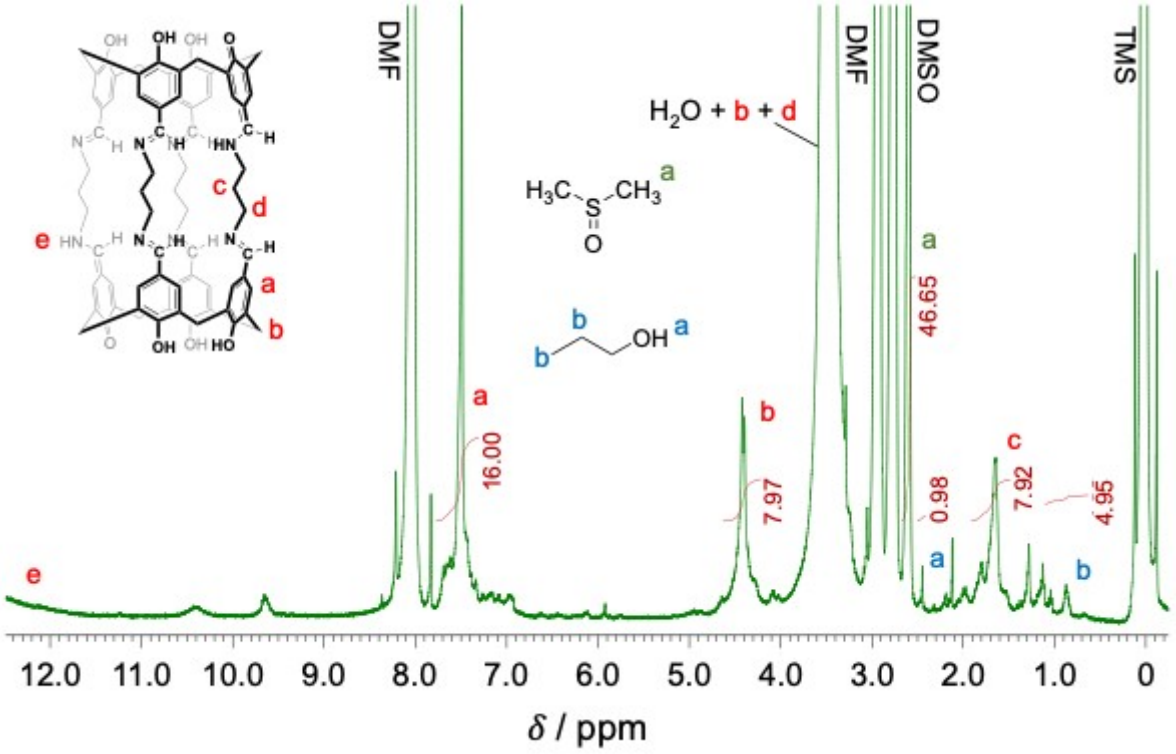


Fig. S15. ^{1}H NMR spectrum of cage molecule DMSO and 1-PrOH inclusion complex (δ from TMS; DMF-d_7, 298K, 500 MHz): the integration ratio indicates the presence of seven DMSO molecules and one 1-PrOH molecule.

3. References

S1. T. D. Guo, Q. Y. Zheng, L. M. Yang and Z. T. Huang, *J*, *Phenom*. *Macrocycl. Chem*., 2000, **36**, 327–333.

S2. Mugnoli, A., Z. Kristallogr. *Suppl*., 1992, **6**, 530.