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Supplementary Material

Halogenation of calix[4]arenes by $[I(py)2]I_3 \cdot 2I_2$

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Supporting Information

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1) Selected analytical data for compound 2 (tetra-*p*-iodo-calix[4]arene).

2) Synthesis and characterization data for compound 3 (25-[3-((2‘-Methoxy-6‘-methylphenol)imino)propoxy]-26,27,28-trihydroxy-calix[4]arene).

3) Selected analytical data for compound 4 (5,11,17-Triiodo-25-[3-((2′-methoxy-6′-methylphenol)imino)propoxy]-26,27,28-trihydroxy-calix[4]arene).

1) Selected analytical data for compound 2 (tetra-*p*-iodo-calix[4]arene).

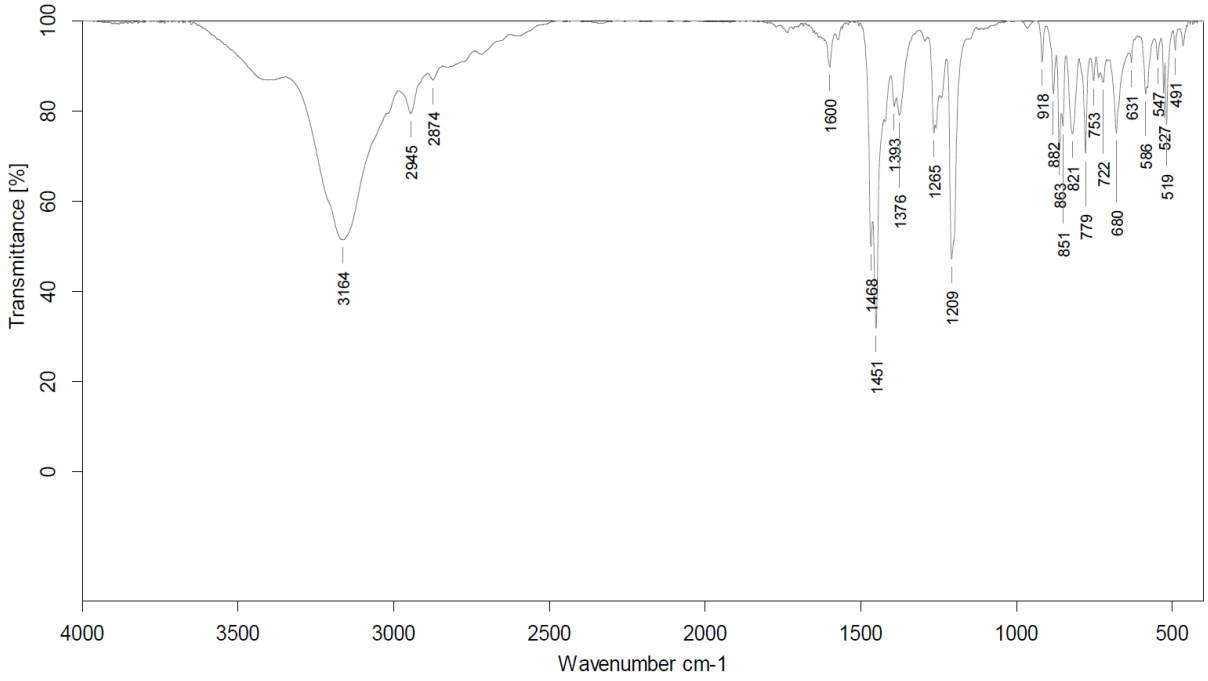


Figure S1. Infrared spectrum for **2**.

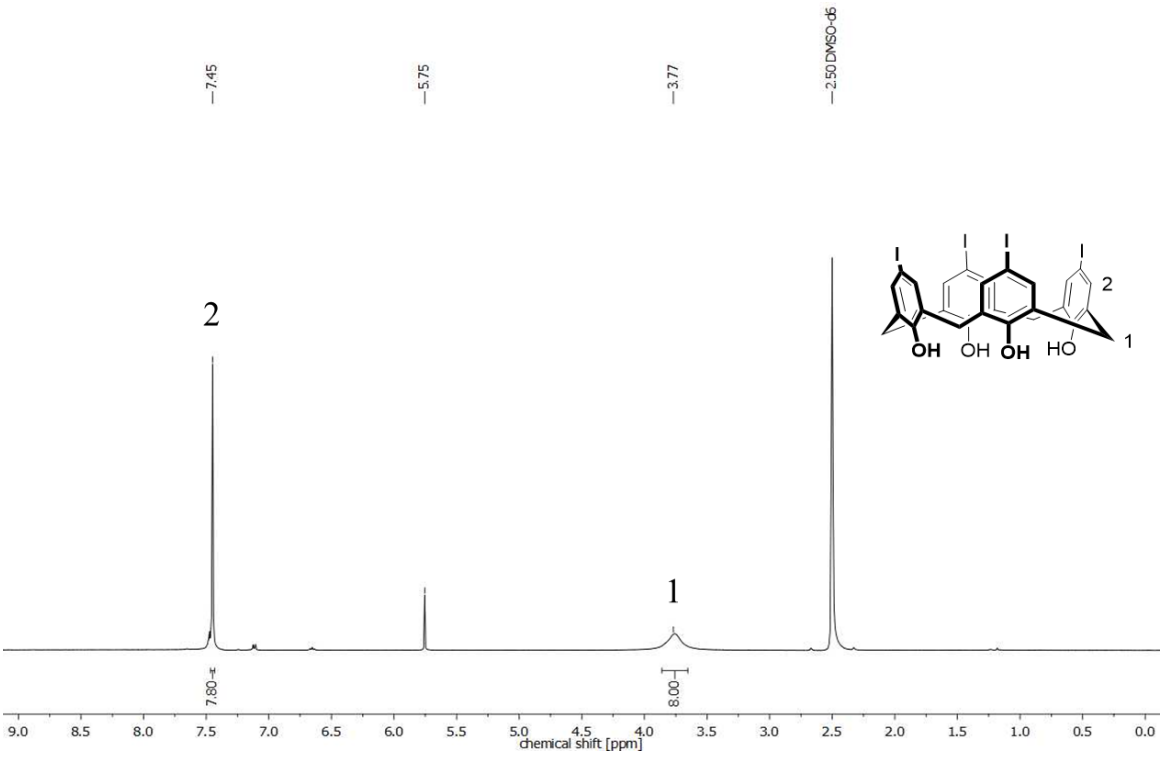
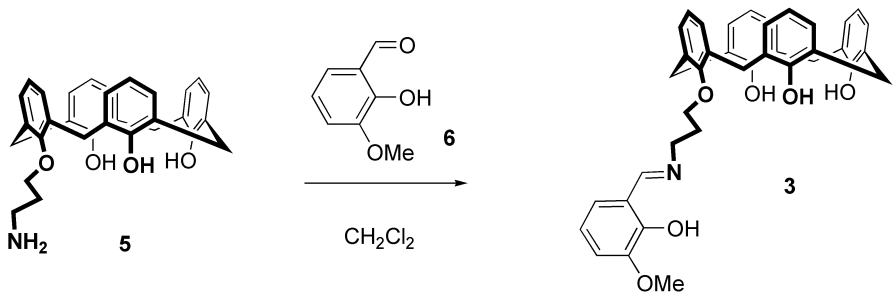


Figure S2. ^{1}H NMR spectrum of **2** in DMSO-d^{6} at ambient temperature.

2. Synthesis and characterization data for compound 3 (25-[3-((2‘-Methoxy-6‘-methylphenol)imino)propoxy]-26,27,28-trihydroxy-calix[4]arene).



To a solution of calix[4]arene **5**[1] (400 mg, 0.831 mmol, 1.00 eq.) in EtOH (200 mL) was added o-vanilline (**6**, 139 mg, 0.914 mmol, 1.10 eq.) and an excess of solid $MgSO_4$. The suspension was refluxed for 5 h, filtered and evaporated to dryness. The remaining solid was triturated with MeOH under sonication, filtered, washed with cold MeOH and dried at 80 °C to give 371 mg (73 %) of **3** as a white solid. m.p. 263 °C (decomp.). ^{1}H-NMR (300 MHz, CD_2Cl_2, see Fig. S4 for labeling scheme): δ 2.55 (p, 2H, ^3J = 6.4 Hz, CH_2, C^{30}), 3.47-3.50 (m, 4H, CH_{eq}H, $C^{2/20}$, $C^{8/14}$), 3.87 (s, 1H, O-CH_3, C^{39}), 4.17 (t, 2H, ^3J = 6.5 Hz, CH_2N, C^{31}), 4.24-4.28 (m, 4H, CHH_{ax}, OCH_2, C^{29}, $C^{8/14}$), 4.33 (d, 2H, 2J = 13.1 Hz, CHH_{ax}, $C^{2/20}$), 6.66-6.72 (m, 3H, *para* ArH, C^{11}, $C^{5/17}$), 6.42 (t, 1H, ^3J = 7.9 Hz, *para* ArH, C^{23}), 6.86-6.96 (m, 3H, ArH, $C^{34,35,36}$), 7.00-7.10 (m, 8H $C^{10/12}$, $C^{6/16}$, $C^{4/18}$, $C^{22/24}$), 8.66 (s, 1H, N=CH, C^{32}). ^{13}C{^{1}H}-NMR (100 MHz, DMSO-d_6, see Fig. S5 for labeling scheme): δ 30.37 (CH_2, C^{30}), 31.11 (CH_2, $C^{2/20}$), 31.70 (CH_2, $C^{8/14}$), 54.35 (CH_2N, C^{31}), 55.72 (CH_3, C^{39}), 73.35 (OCH_2, C^{29}), 114.69 (Ar^C, C^{11}), 117.61 (Ar^C, $C^{5/17}$), 118.32 (Ar^{COR}, C^{37}), 119.00 (Ar^C, C^{35}), 123.17 (Ar^C, C^{23}), 124.60 (Ar^C, C^{34}), 128.08 (Ar^C, $C^{4/18}$), 128.28 (Ar^C, $C^{6/16}$), 128.33 (Ar^C, $C^{10/12}$), 128.64 (Ar^C, $C^{9/13}$), 128.72 (Ar^C, $C^{22/24}$), 128.84 (Ar^C, C^{36}), 128.88 (Ar^C, $C^{7/15}$, $C^{3/19}$), 133.94 (Ar^C, $C^{1/21}$), 148.09 (Ar^{COH}, C^{38}), 151.92 (Ar^{COH}, C^{27}), 152.60 (Ar^{COH}, $C^{26/28}$), 152.65 (Ar^C, C^{33}), 152.76 (Ar^{COR}, C^{25}), 166.79 (C=N, C^{32}). ATR-IR (ZnSe) ν/cm^{-1}: 3314 (s, br, ν O–H), 3029 (w, br, ν O–H), 2937 (w), 2876 (w), 1637 (m, ν C=N), 1592 (w, ν C=C), 1465 (s, ν C=C), 1381 (w, ν C=C), 1357 (w), 1250 (m), 1193 (m), 1151 (w), 1084 (m), 1049 (m), 971 (w), 918

(w), 842 (w), 755 (m), 732 (m). UV-vis (CH_2Cl_2/MeOH 3:1 v/v): λ_{max} [nm] (ε [$M^{-1}cm^{-1}$] = 230 (22760), 267 (11875), 332 (2009), 418 (955). *m/z* (ESI negative mode, MeCN): $C_{39}H_{37}NO_6$ (615.3) $[M\text{-}H^+]^-$ calcd: 614.3; found 614.3. Elemental analysis for $C_{39}H_{37}NO_6 \cdot 0.5H_2O$ (615.70+9.01) calc. C 74.98, H 6.13, N 2.24, %; found. C 75.26, H 5.99, N 4.89 %. This compound was additionally characterized by X-ray crystallography.

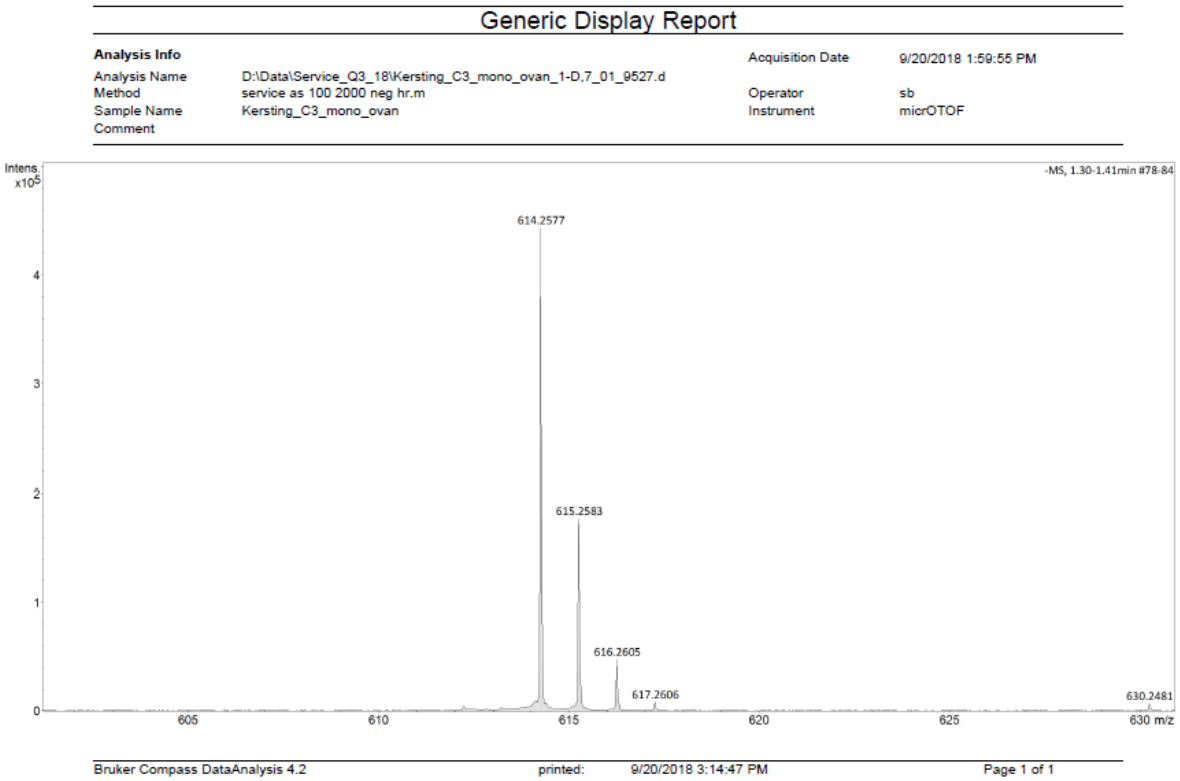


Figure S3. ESI-MS spectrum for **3** (negative mode, MeCN).

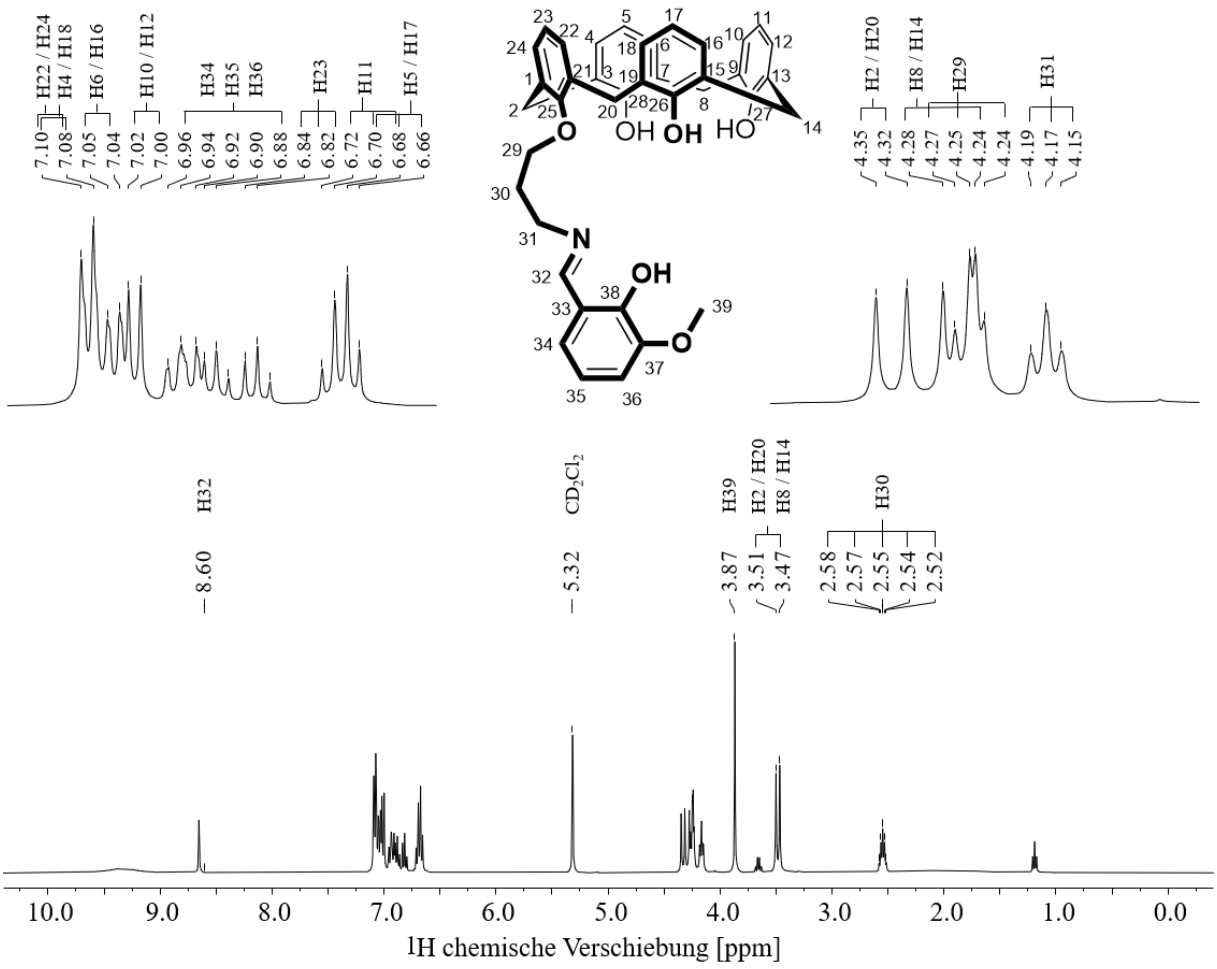


Figure S4. ^{1}H NMR spectrum for **3** in CD_2Cl_2. Inset: Labeling scheme for compound **3** used to assign NMR chemical shifts.

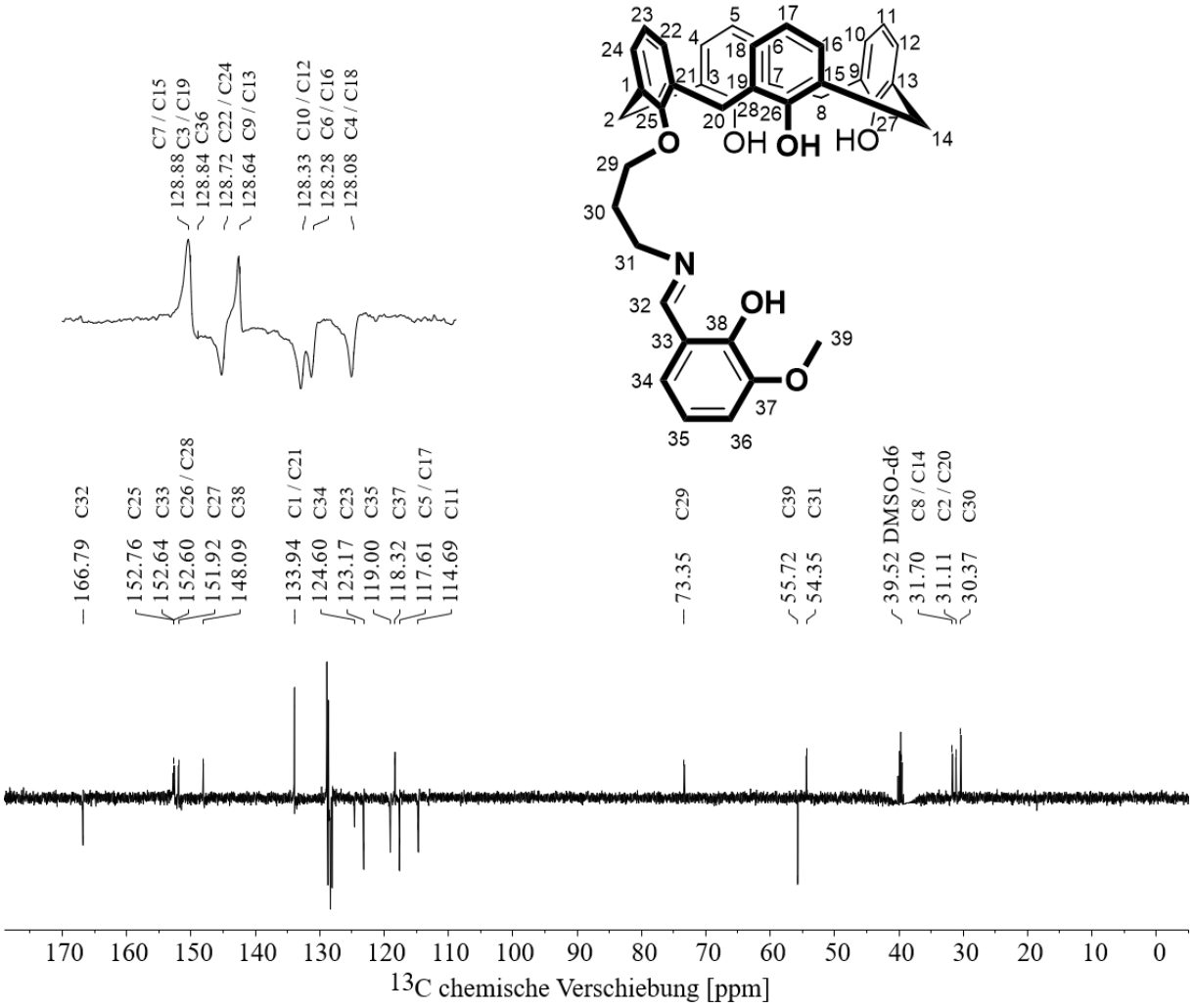


Figure S5. APT spectrum of **3** in CD_2Cl_2 at ambient temperature. Inset: Labeling scheme for compound **3** used to assign NMR chemical shifts.

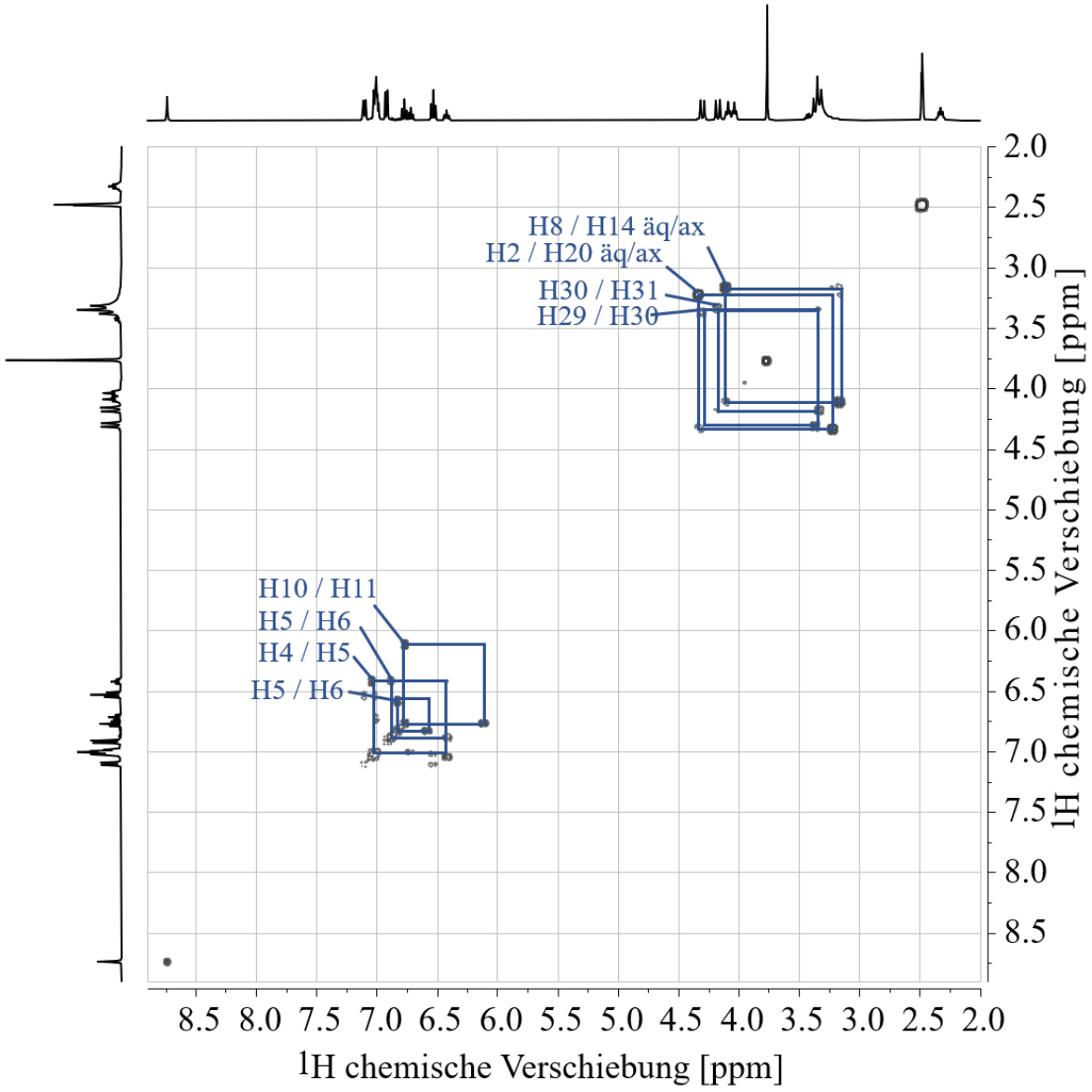


Figure S6. $^{1}H,^{1}H$ COSY spectrum of **3** in CD_2Cl_2 at ambient temperature. See figure SX for assignment of atom labels.

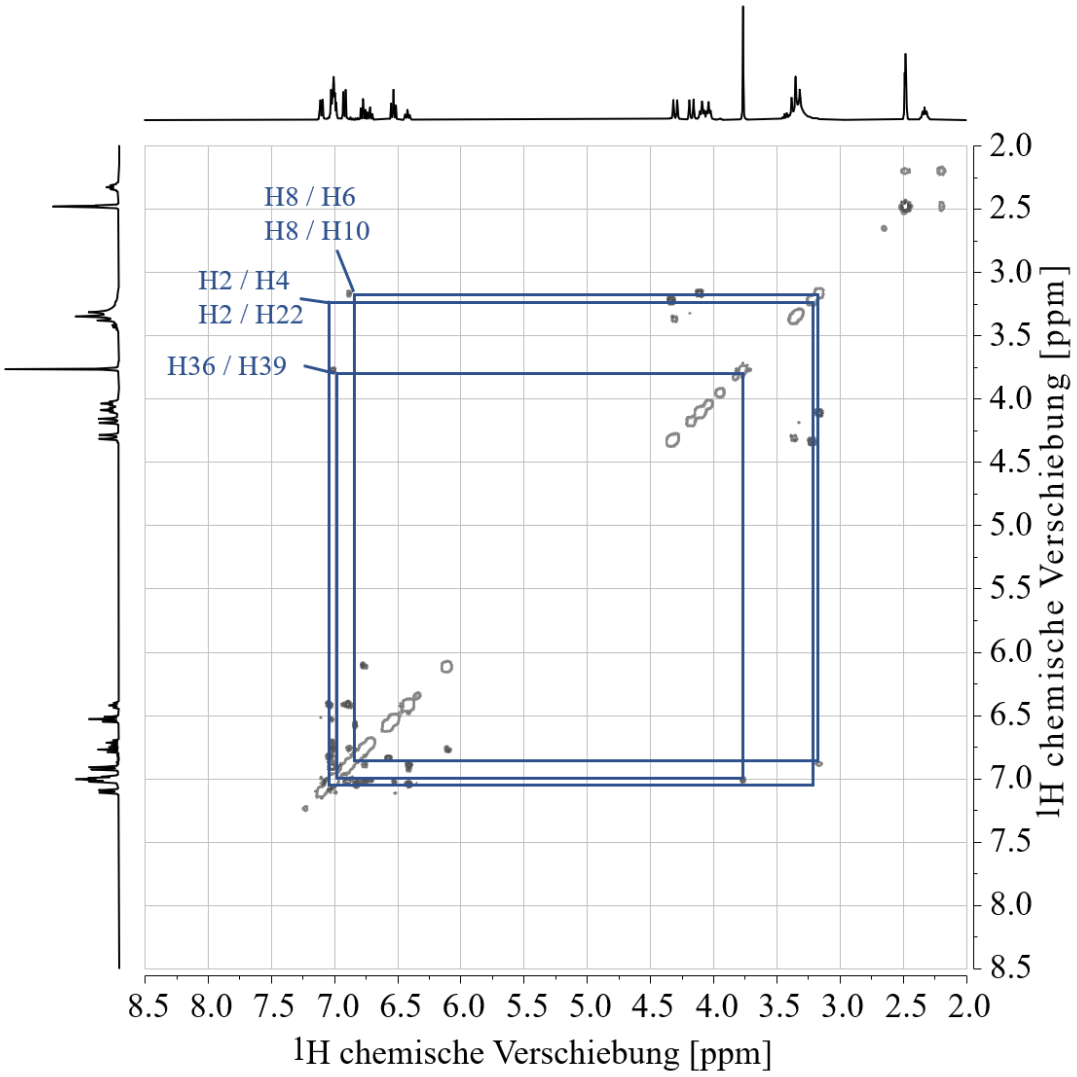


Figure S7. $^{1}H,^{1}H$ NOESY spectrum of **3** in CD_2Cl_2 at ambient temperature. See figure SX for atom labeling.

3) Selected analytical data for compound 4 (5,11,17-Triiodo-25-[3-((2′-methoxy-6′-methylphenol)imino)propoxy]-26,27,28-trihydroxy-calix[4]arene).

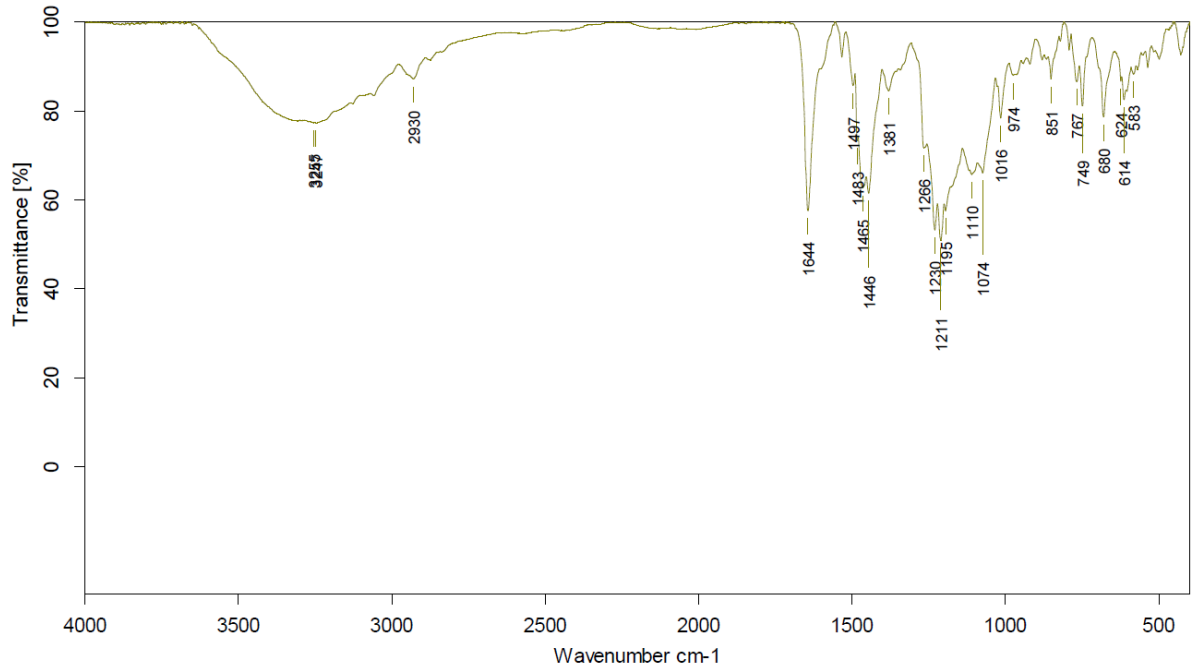


Figure S8. ATR infrared spectrum of **4**.

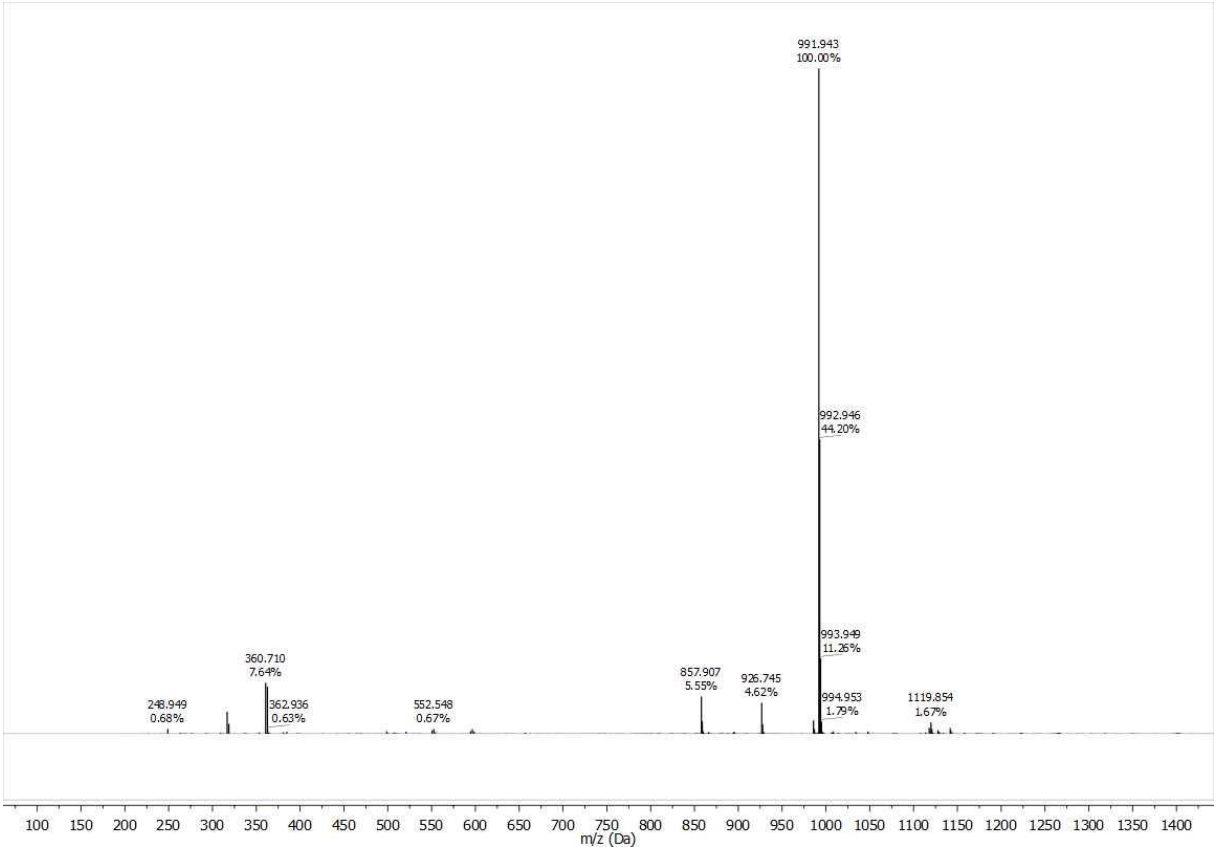


Figure S9. ESI mass spectrum of 4.

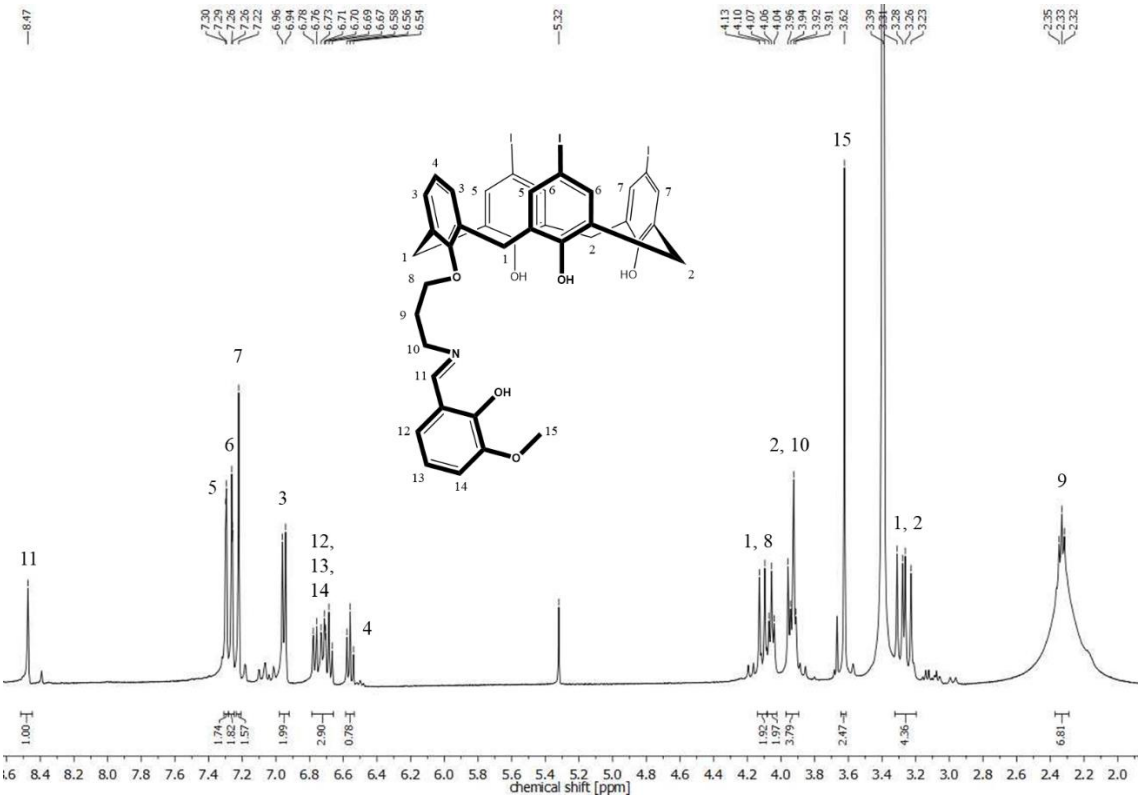


Figure S10. ^{1}H NMR spectrum of **4** in CD_2Cl_2 at ambient temperature.

References

1 P. Hahn, S. Ullmann, A. Kahnt, B. Abel, B. Kersting, *Inorg. Chim. Acta* **2021**, *514*, 119983.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv-0510

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv-0510

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Bond precision:   C-C = 0.0295 A          Wavelength=1.54186

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                  alpha=90         beta=95.279(4)      gamma=90
Temperature:      180 K
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Hall group	-P 2ybc	-P 2ybc
Moiety formula	C39 H34 I3 N O6	C39 H34 I3 N O6
Sum formula	C39 H34 I3 N O6	C39 H34 I3 N O6
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Dx,g cm-3	1.781	1.781
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Mu (mm-1)	20.257	20.257
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F000'	1929.90	
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S = 1.059                 Npar= 203
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.3580

Author Response: Due to technical reasons the measurement was interupted and the dataset is incomplete. We were not able to grow well diffracting single crystals again.

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) ..... 39 Report
C1 C2 C3 C4 C5 etc.

Author Response: Due to technical reasons the measurement was interupted and the dataset is incomplete. We were not able to grow well diffracting single crystals again.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.956 Why?

Author Response: Due to technical reasons the measurement was interupted and the dataset is incomplete. We were not able to grow well diffracting single crystals again.

PLAT088_ALERT_3_B Poor Data / Parameter Ratio ..... 6.70 Note

Author Response: Due to technical reasons the measurement was interupted and the dataset is incomplete. We were not able to grow well diffracting single crystals again.

PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.02951 Ang.

Author Response: Due to technical reasons the measurement was interupted and the dataset is incomplete. We were not able to grow well diffracting single crystals again.

Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 4.7 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 5.4 Ratio

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PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C37 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C38 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C34 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C36 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.1 Note
PLAT601_ALERT_2_C Unit Cell Contains Solvent Accessible VOIDS of .         36 Ang**3
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.358         62 Report
PLAT971_ALERT_2_C Check Calcd Resid. Dens.  1.54Ang From I1              2.25 eA-3
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Alert level G

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                                             x,3/2-y,1/2+z  =      4_576 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  I3       ..C26      .       3.41 Ang.
                                             x,1/2-y,1/2+z  =      4_566 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        80% Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.5 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
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  2 ALERT level A = Most likely a serious problem - resolve or explain
  3 ALERT level B = A potentially serious problem, consider carefully
 11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  7 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 14 ALERT type 2 Indicator that the structure model may be wrong or deficient
  8 ALERT type 3 Indicator that the structure quality may be low
  0 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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Datablock sv-0510 - ellipsoid plot