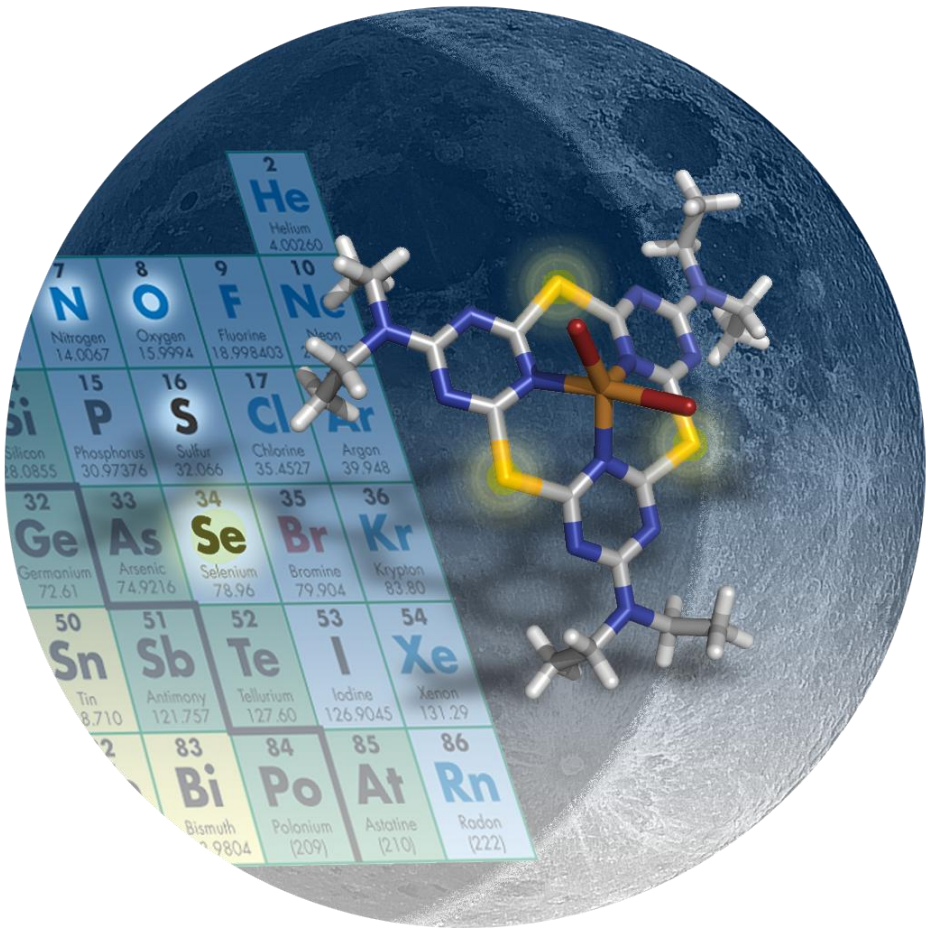
Electronic Supplementary Information

Selenacalix[3]triazines: Synthesis and Host–Guest Chemistry

Joice Thomas,[a] Wim Van Rossom,[a] Kristof Van Hecke,[b] Luc Van Meervelt,[b] Mario Smet,[a] Wouter Maes[a,c] and Wim Dehaen*[,a]

[a] *Molecular Design and Synthesis, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium*
wim.dehaen@chem.kuleuven.be; Fax: +32 16327990; Tel.: +32 16327439
[b] *Biomolecular Architecture, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium*
[c] *Design & Synthesis of Organic Semiconductors (DSOS), Institute for Materials Research (IMO), Hasselt University, Universitaire Campus, Agoralaan – Building D, 3590 Diepenbeek, Belgium*



Inspired by the beautiful moon goddess “Selene“, the heteracalixarene series (N/O/S) has been expanded with Se-bridged cyclotrimeric macrocycles. Selenacalix[3]triazines show peculiar supramolecular features. The N tridentate binding pocket is capable of coordinating both (Cu) metal salts and anions.

Table of contents

1. General experimental methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz or Bruker AMX 400 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signals (^{13}C).[1] ^{77}Se NMR spectra were recorded using Ph_2Se_2 in $CDCl_3$ as an external reference (δ = 463 ppm).[2] Mass spectra were obtained using a HP5989A apparatus (CI, 70 eV ionisation energy) with Apollo 300 data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000) or a Bruker Daltonics Apex2 FT-ICR instrument (performed in the ESI mode at a resolution of 60000). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70–230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Reaction solvents (THF, ethanol and acetone) were used as received from commercial sources.
Tetrabutylammonium salts were purchased from Sigma-Aldrich and dried overnight under vacuum at 40 °C prior to the spectrophotometric measurements. UV/Vis spectra were measured using an ultraviolet–visible spectrophotometer Perkin-Elmer Lambda40 with a quartz cuvette (path length 1 cm) at 293 K. A stock solution of 1.0×10^{-5} M of the host compound **2c** was prepared in acetonitrile (dried on molecular sieves 4 Å). Solutions of 1.0×10^{-3} M of the tetrabutylammonium salts of the respective anions were prepared with the host stock solution to maintain a constant host concentration throughout the whole titration experiment.

Safety precautions

The most convenient procedure to prepare NaSeH involves reduction of Se with $NaBH_4$. It allows the rapid and easy preparation of NaSeH without the necessity of generating dangerously toxic H_2Se.
Handling, storage, and precautions while dealing with NaSeH: unstable compound, decomposes in moist air with the formation of polyselenides and precipitation of Se. It should be used directly as prepared in solution or suspension without isolation. Use in a fume hood.[3]

2. Experimental and characterization data

Triazine building blocks

2-Butyl-4,6-dichloro-1,3,5-triazine (1a). *n*-Butylmagnesium bromide (56 mL, 1M in THF) was added dropwise to a cold (0 °C) solution of cyanuric chloride (10.0 g, 54.3 mmol) in anhydrous THF (100 mL) over a period of 5 min. The temperature was gradually increased to RT and stirring was continued for another 5 h. The reaction was quenched by careful addition of NH_4Cl (aq). CH_2Cl_2 (200 mL) was added, the organic layer was separated and washed with distilled water (100 mL), dried over $MgSO_4$, filtered and evaporated to dryness to afford the crude product. Purification by column chromatography (silica, eluent CH_2Cl_2–heptane 4:1) afforded triazine derivative **1a** (9.0 g; 80%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (t, J = 7.7 Hz, 2H), 1.88–1.74 (m, 2H), 1.42 (s, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 171.8, 38.5 (CH_2), 29.6 (CH_2), 22.5 (CH_2), 13.8 (CH_3); MS (ESI$^+$) *m/z* 206 [MH$^+$]; HRMS (EI) calcd for $C_7H_9Cl_2N_3$ [M^+]: 205.0174; found: *m/z* 205.0159.[4]

1 H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.
2 H. Duddeck, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1995, **27**, 1.
3 J. Mochowski, L. Syper, *Sodium Hydrogen Selenide* in *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, 2001.
4 Both the calculated and experimental masses refer to the 100% intensity peak of the isotopic distribution.

2,4-Dichloro-6-phenoxy-1,3,5-triazine (1b). This compound has been prepared according to the procedure reported by Götz *et al*.[5] Material identity was confirmed by MS, ^{1}H and ^{13}C NMR.
4,6-Dichloro-*N*,*N*-diethyl-1,3,5-triazine-2-amine (1c). This compound has been prepared according to the procedure reported by Hermon *et al*.[6] Material identity was confirmed by MS, ^{1}H and ^{13}C NMR.

Selenacalix[3]triazines

4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-tributyl-2,8,14-triselenacalix[3]arene (2a). Dichlorotriazine precursor **1a** (0.100 g, 0.48 mmol) was dissolved in acetone (140 mL) and the solution was degassed by purging with Ar for 10 min. A solution of NaSeH (0.48 mmol, 1 equiv) in distilled H_2O (4 mL) was freshly prepared according to a reported procedure[7] and added dropwise by syringe into the flask containing **1a** at -78 °C. The temperature was gradually increased to RT over 1 h. After stirring the resulting mixture for another 12 h, the reaction mixture was added to water (40 mL) and the precipitate formed was filtered off and dried in vacuum to afford analytically pure product **2a** (0.078 g; 75%) as an off-white solid. mp 73−74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77 (t, J = 7.7 Hz, 6H), 1.77 (q, J = 7.6 Hz, 6H), 1.40 (s, J = 7.4 Hz, 6H), 0.95 (t, J = 7.3 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 178.0, 38.1 (CH_2), 29.8 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ 559; MS (ESI$^+$) *m/z* 643.2 [*M*+H]$^+$; FTMS (ESI$^+$) calcd for $C_{21}H_{27}N_9Se_3Na$ [*M*+Na]$^+$: 665.9793; found: *m/z* 665.9784.
4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-triphenoxy-2,8,14-triselenacalix[3]arene (2b). Dichlorotriazine precursor **1b** (0.200 g, 0.82 mmol) was dissolved in acetone (70 mL) and the solution was degassed by purging with Ar for 10 min. A solution of NaSeH (0.82 mmol, 1 equiv) in distilled water (4 mL) was freshly prepared according to a reported procedure[7] and added dropwise by syringe into the flask containing **1b** at -78 °C. The temperature was gradually increased to RT over 1 h. After stirring the resulting mixture for another 12 h, water (70 mL) was added and the precipitate formed was filtered off and dried in vacuum to afford analytically pure product **2b** (0.145 g; 70%) as an off-white solid. mp 222−223 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (t, J = 7.8 Hz, 6H), 7.33–7.26 (m, 3H), 7.15 (d, J = 8.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9, 166.8, 151.3, 129.9 (CH), 126.7 (CH), 121.3 (CH); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ 577; MS (ESI$^+$) *m/z* 751.5 [*M*+H]$^+$; FTMS (ESI$^+$) calcd for $C_{27}H_{15}N_9O_3Se_3Na$ [*M*+Na]$^+$: 773.8703; found: *m/z* 773.8704.
4,6,10,12,16,18,19,20,21-Nonaaza-5,11,17-tris(*N*,*N*-diethylamino)-2,8,14-triselenacalix[3]arene (2c). Dichlorotriazine precursor **1c** (0.200 g, 0.90 mmol) was dissolved in acetone (50 mL) and the solution was degassed by purging with Ar for 10 min. A solution of NaSeH (1.05 equiv) in distilled water (3 mL) was freshly prepared according to the reported procedure[7] and added dropwise by syringe into the flask containing **1c** at 0 °C. The temperature was gradually increased to 40 °C and stirring was continued for 2 days. The reaction mixture was cooled to RT, water (50 mL) was added, and the resulting precipitate was filtered off and dried under vacuum to afford crude product **2c** (0.150 g; 72%) as an off-white solid. The precipitated compound (150 mg) was redissolved in a mixture of CH_2Cl_2 and CH_3CN (2:3, 20 mL) and crystals of the pure compound **2c** (0.115 g; 55%) were obtained within one day by slow evaporation at ambient temperature. mp 175−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60–3.48 (m, 12H), 1.15 (t, J = 6.8 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 160.2, 41.7 (CH_2), 12.8 (CH_3); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ 549 ppm; MS (ESI$^+$) *m/z* 688.2 [*M*+H]$^+$; FTMS (ESI$^+$) calcd for $C_{21}H_{30}N_{12}Se_3$ [*M*+Na]$^+$: 688.0228; found: *m/z* 688.0330; UV/Vis (CH_3CN) λ_{max} (log ε) 259 (4.498).

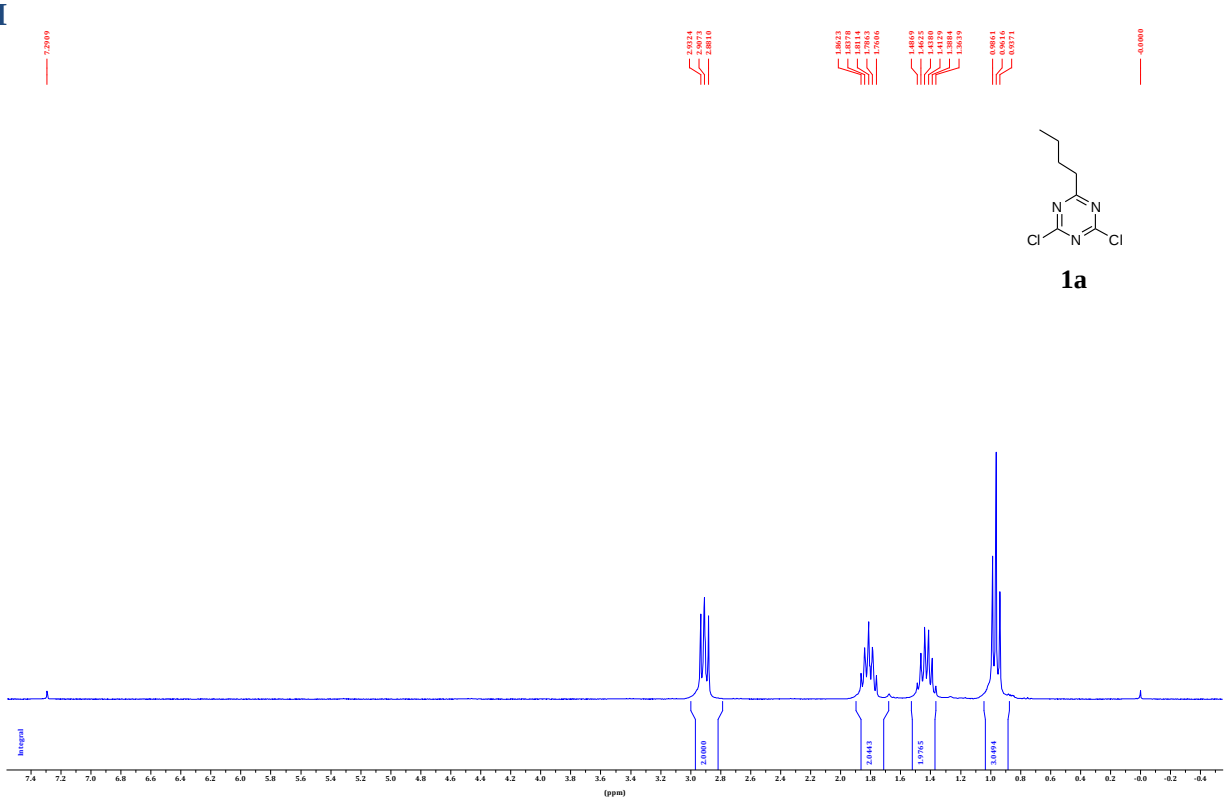
5 R. J. Götz, A. Robertazzi, I. Mutikainen, U. Turpeinen, P. Gamez, J. Reedijk, *Chem. Commun*., 2008, 3384.
6 T. Hermon, E. Y. Tshuva, *J. Org. Chem.*, 2008, **73**, 5953.
7 D. L. Klayman, T. S. Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 197.

Synthesis of Cu^{II} complex 3c. A solution of selenacalix[3]triazine **2c** (0.050 g, 0.072 mmol) in THF (10 mL) was added to a solution of $CuBr_2$ (0.017 g, 0.072 mmol) in THF (15 mL) at RT and the mixture was stirred for 10 h during which some precipitate was formed. The resulting suspension was evaporated to dryness and washed with diethyl ether to afford the monomeric complex [$CuBr_2$–**2c**] (**3c**) (0.060 g; 94%) as a green solid. mp 230−232 °C; MS (ESI^+) *m/z* 1502 $[2(M\text{-}2Br)]^+$; UV/Vis (CH_3CN) λ_{max} (log ε) 273 (4.785).
X-ray quality single crystals of complex **3c** were obtained by slow evaporation of a CH_2Cl_2/CH_3CN (1:1) solution of **3c** at ambient temperature.

Synthesis of Cu^{I} complex 4c. A solution of selenacalix[3]triazine **2c** (0.050 g, 0.072 mmol) in THF (10 mL) was added to a solution of CuBr (0.011 g, 0.072 mmol) in THF (15 mL) at RT and the mixture was stirred for 10 h during which some precipitate was formed. The resulting suspension was evaporated to dryness and washed with diethyl ether to afford the monomeric complex [CuBr–**2c**] (**4c**) (0.054 g; 91%) as a yellow solid. mp 172−173 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80–3.40 (m, 12H), 1.15 (s_{br}, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 158.3, 42.4 (CH_2), 12.8 (CH_3); ^{77}Se NMR (76.3 MHz, $CDCl_3$) δ 567; MS (ESI^+) *m/z* 751 $[M\text{-}Br]^+$; UV/Vis (CH_3CN) λ_{max} (log ε) 267 (4.830).
X-ray quality single crystals of complex **4c** were obtained by slow evaporation of a CH_2Cl_2/CH_3CN (1:1) solution of **4c** at ambient temperature.

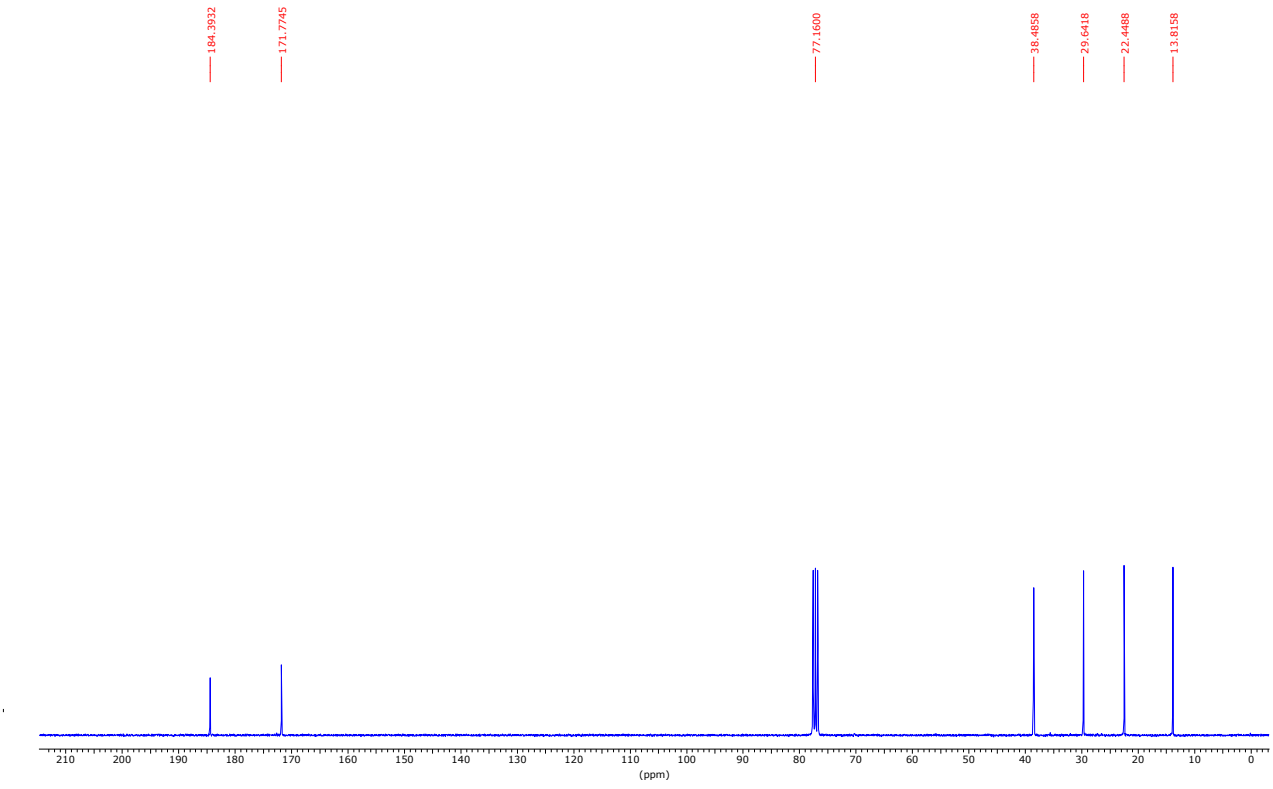
3. ^{1}H ,^{13}C and ^{77}Se NMR spectra for the triazine precursors and selenacalix[3]triazines

^{1}H

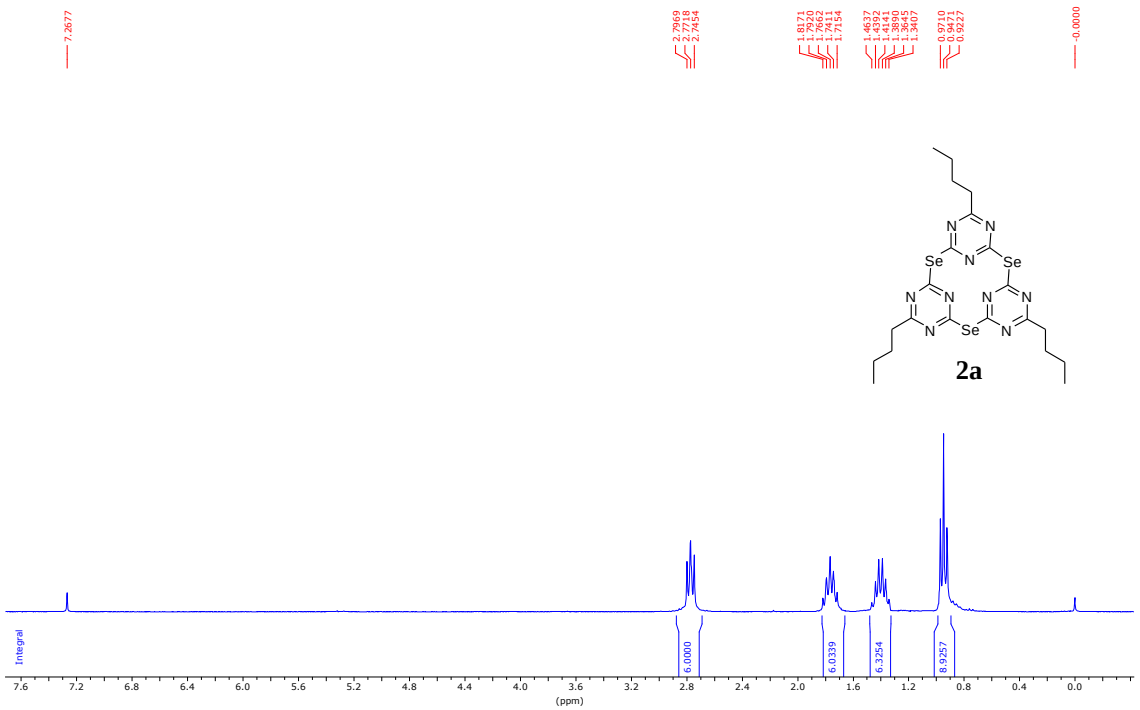


1a

^{13}C

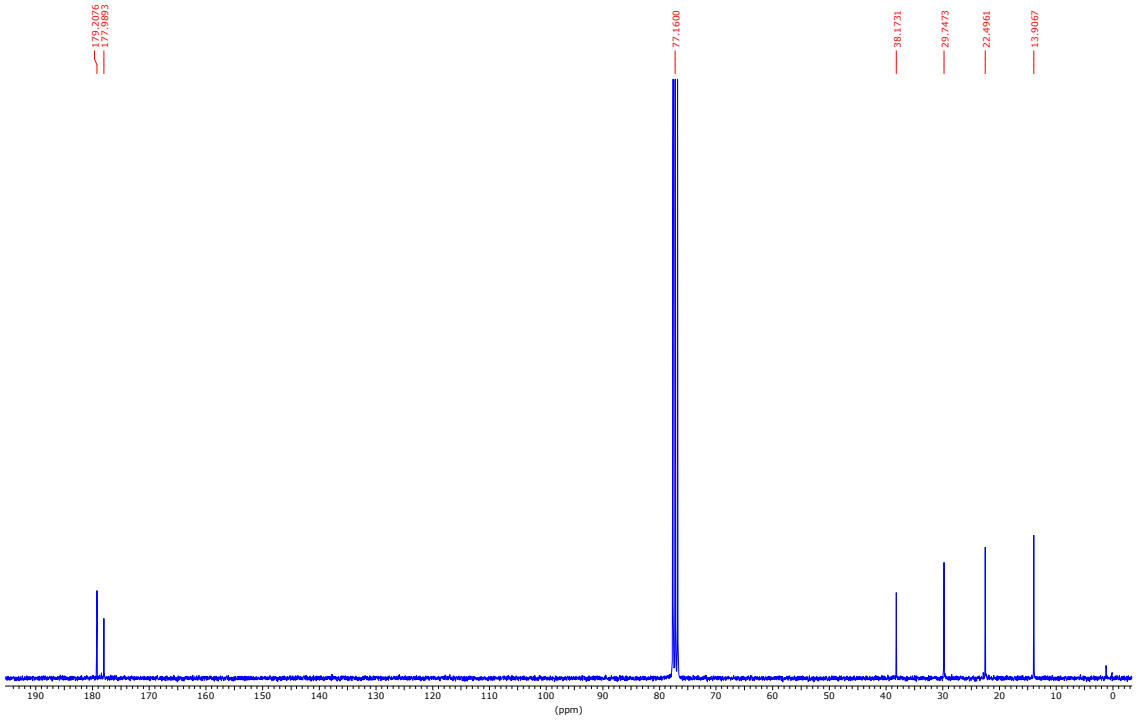


^{1}H

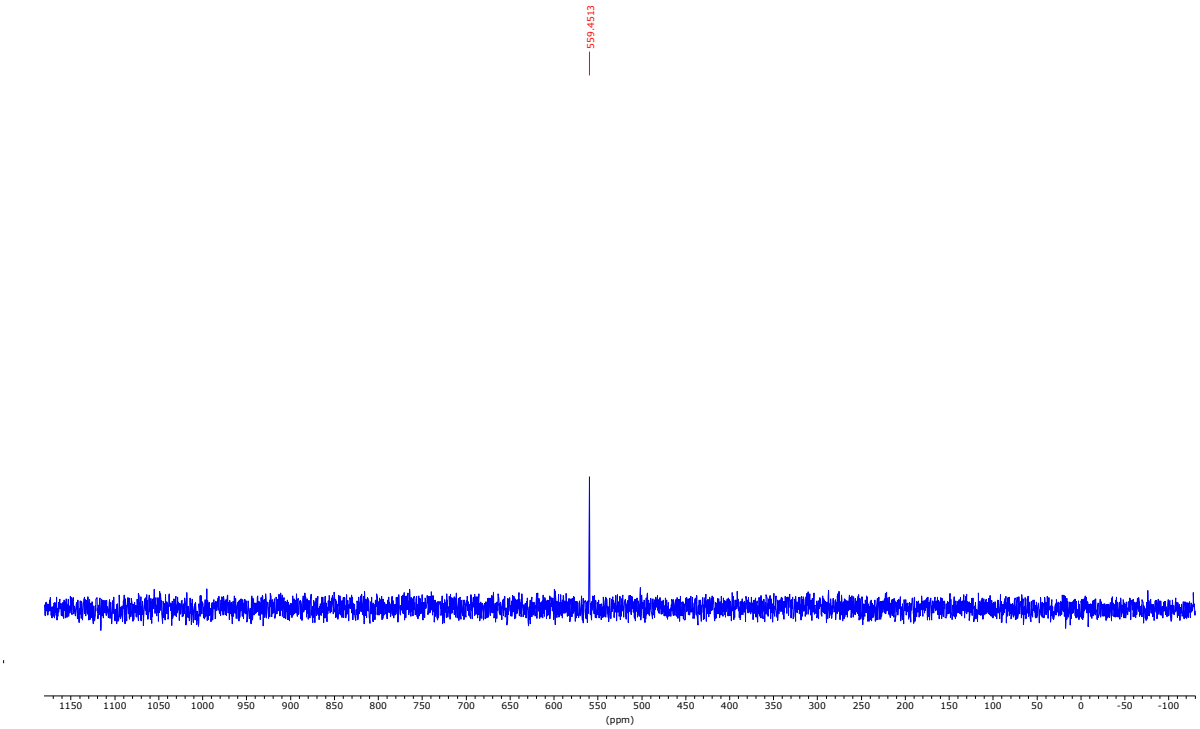

7.2677
2.7969
2.7718
2.7454
1.8171
1.7920
1.7762
1.7411
1.7154
1.4637
1.4432
1.4141
1.3890
1.3645
1.3407
0.9710
0.9471
0.9271
0.9227
-0.0000
Integral
6.0000
6.0339
6.3254
8.9257
(ppm)

2a

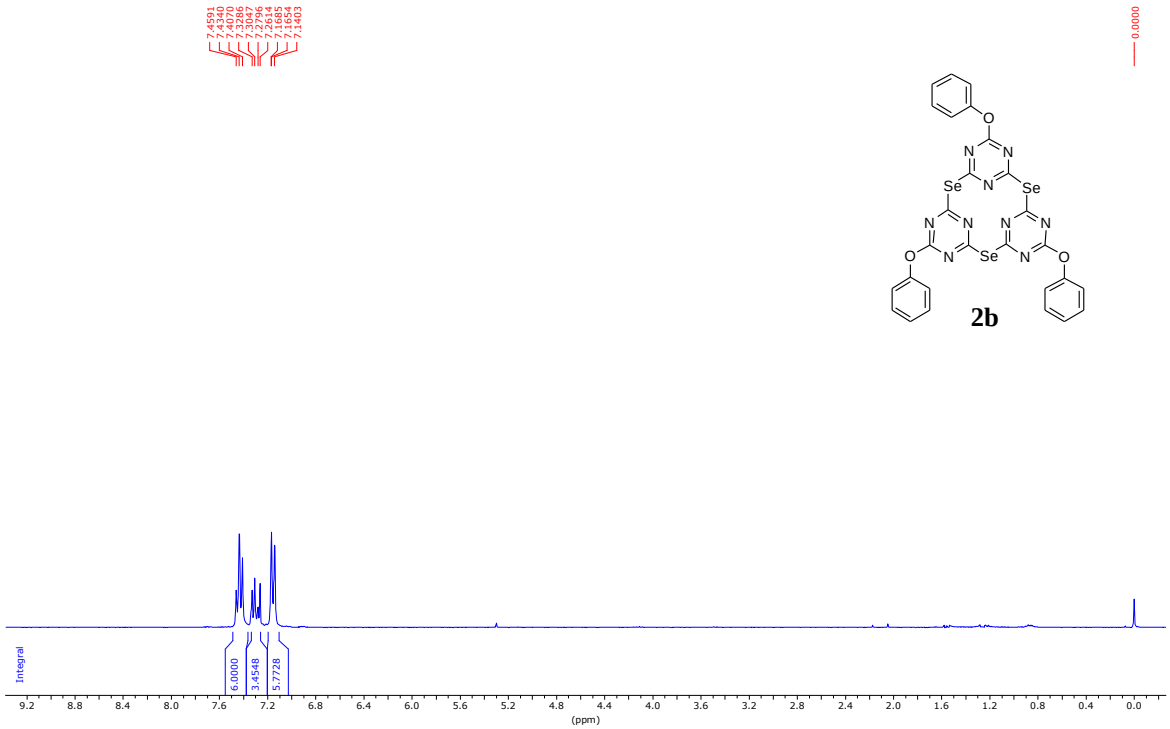
^{13}C


179.2076
177.9893
77.1600
38.1731
29.7473
22.4961
13.9067
(ppm)

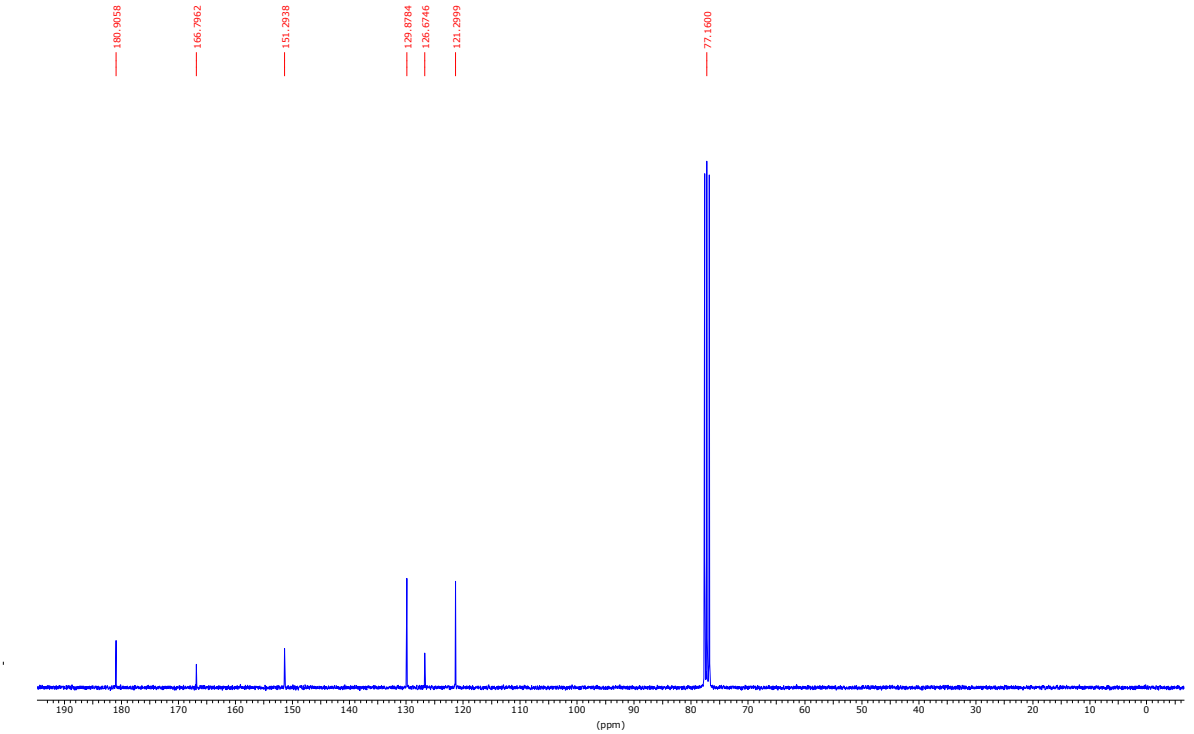
^{77}Se


559.4513
1150 1100 1050 1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100
(ppm)

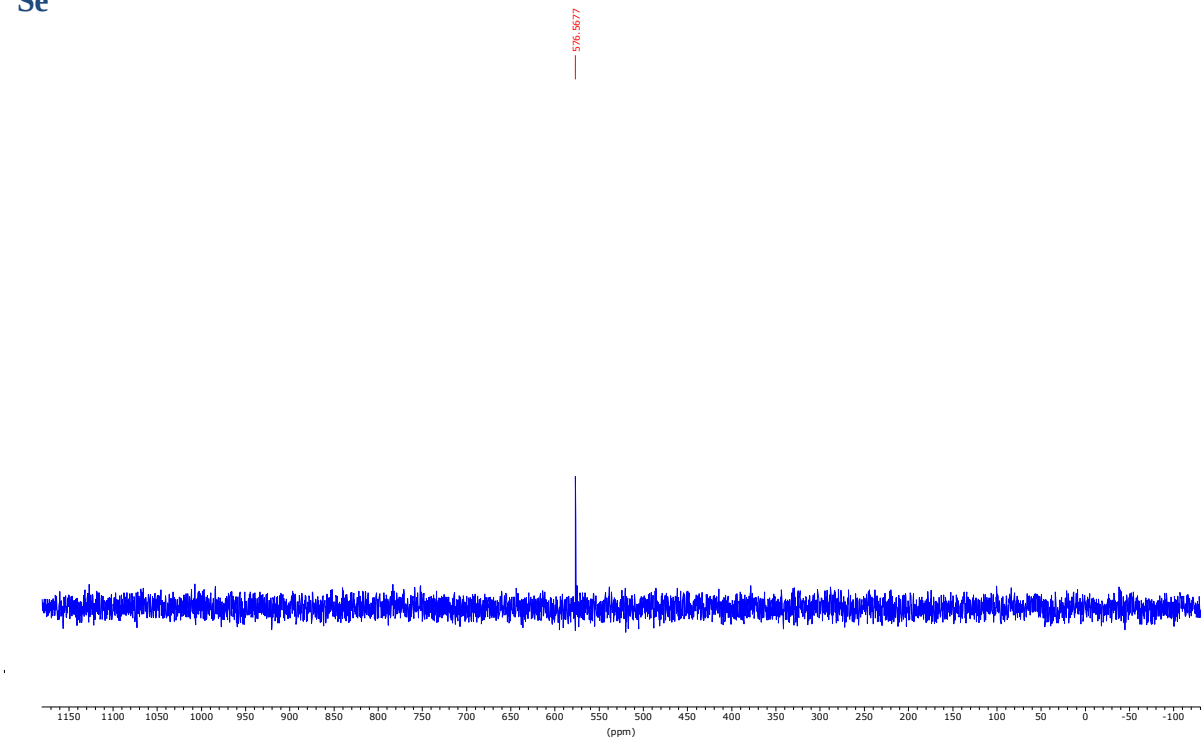
^{1}H


7.4591
7.4340
7.4070
7.3286
7.3067
7.2796
7.2614
7.2485
7.1654
7.1403
0.0000
O
N
Se
2b
Integral
6.0000
3.4548
5.7728
(ppm)

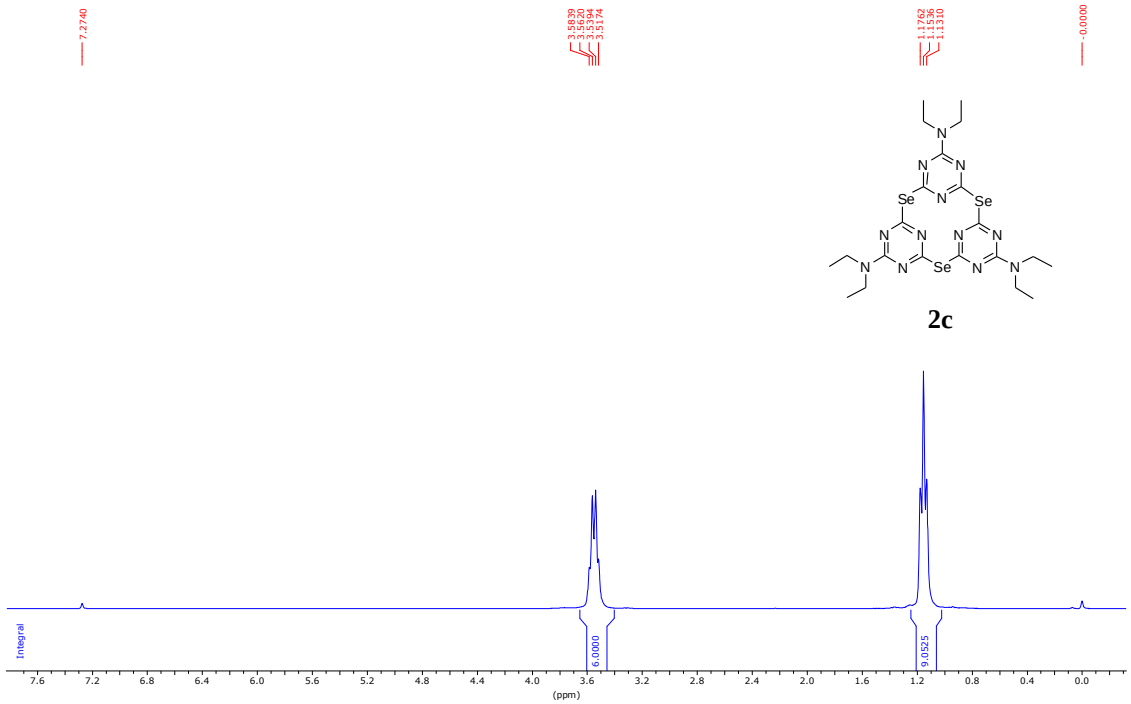
^{13}C


180.9058
166.7962
151.2938
129.8784
126.6746
121.2999
77.1600
(ppm)

^{77}Se

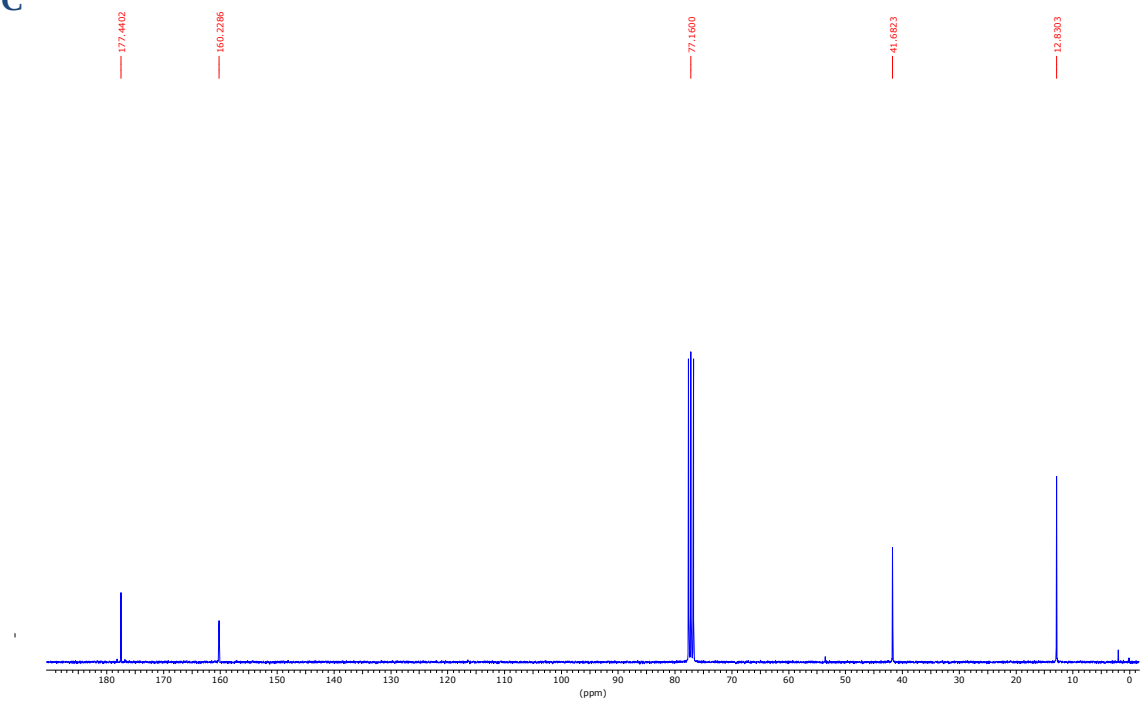

576.5677
1150
1100
1050
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
(ppm)

^{1}H

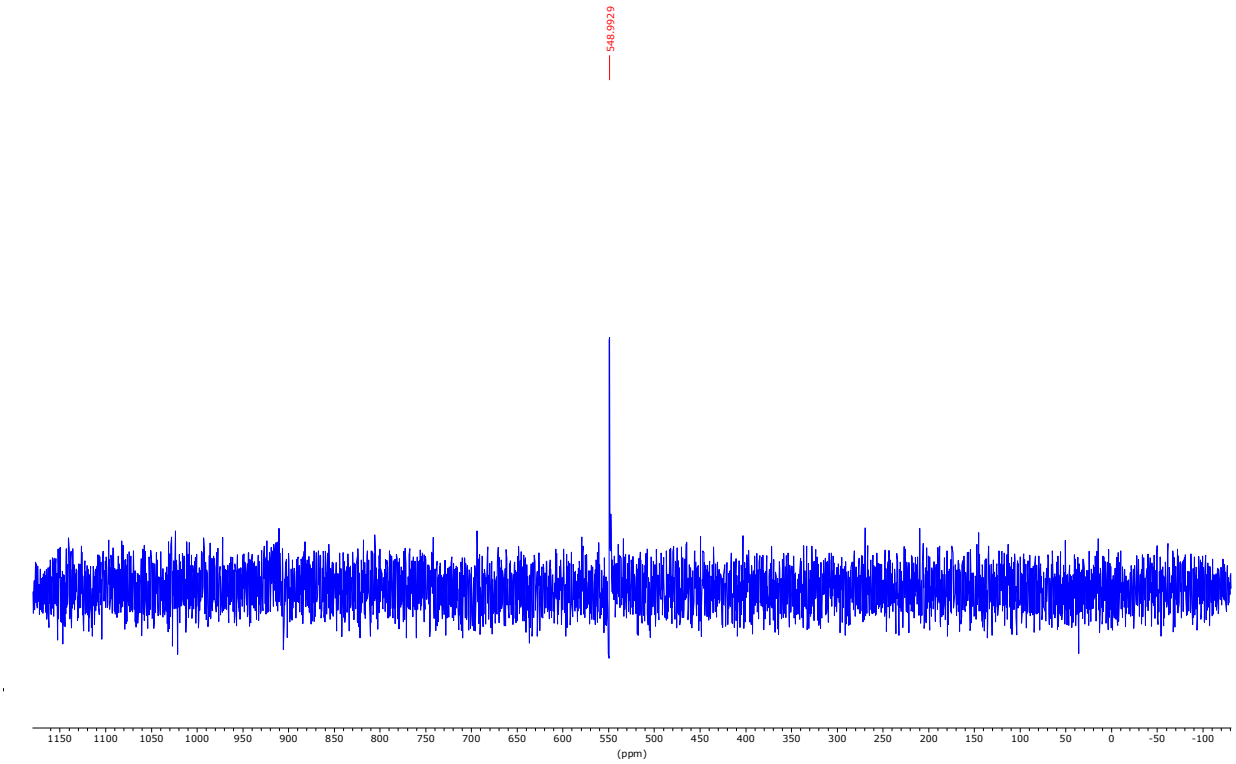

7.2740
3.5839
3.5620
3.5394
3.5174
1.1762
1.1536
1.1310
0.0000
Integral
6.0000
9.0525
7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0
(ppm)

2c

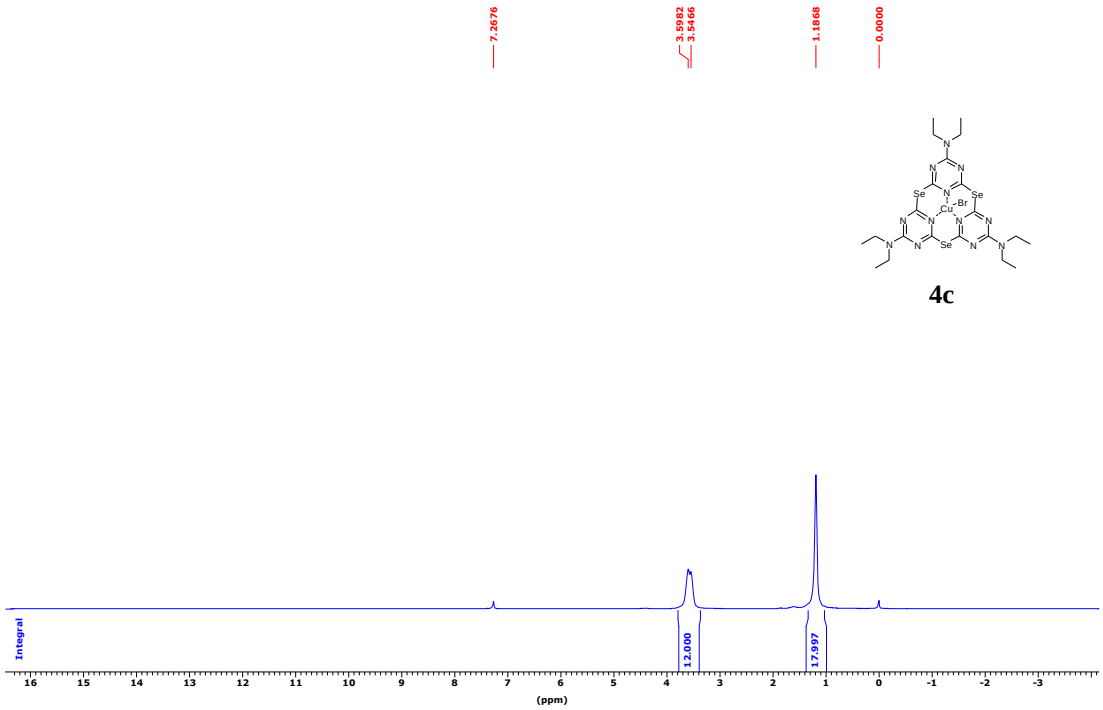
^{13}C


177.4402
160.2286
77.1600
41.6823
12.8303
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

^{77}Se

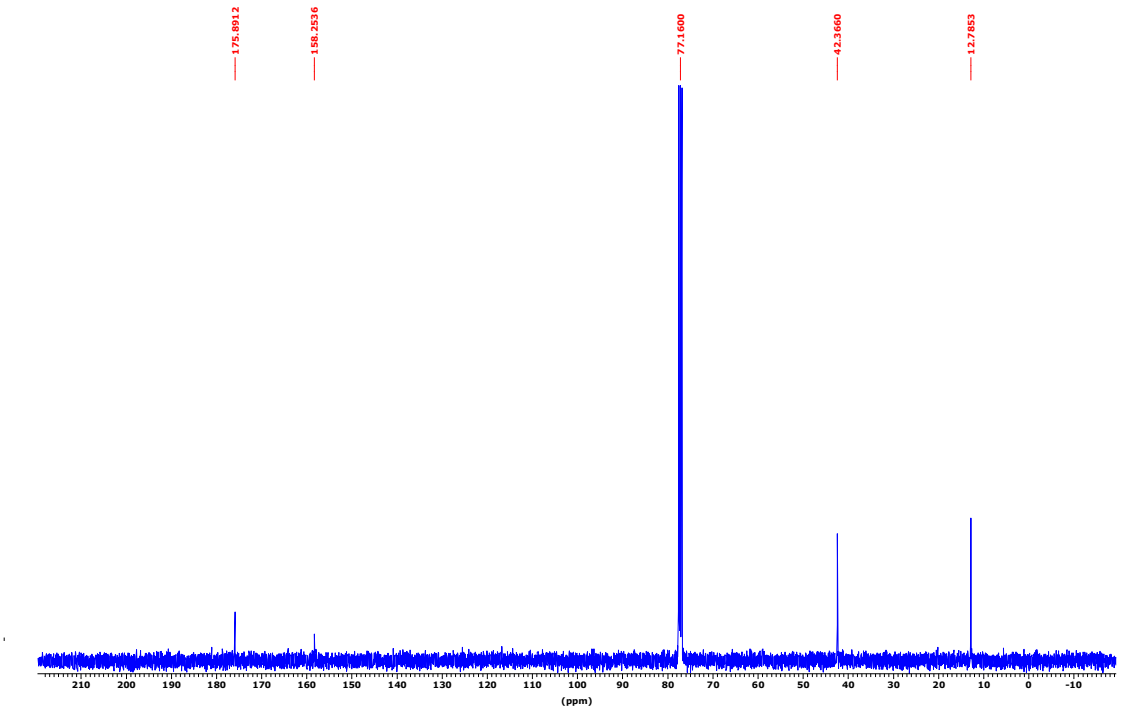

548.9929
1150 1100 1050 1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100
(ppm)

^{1}H

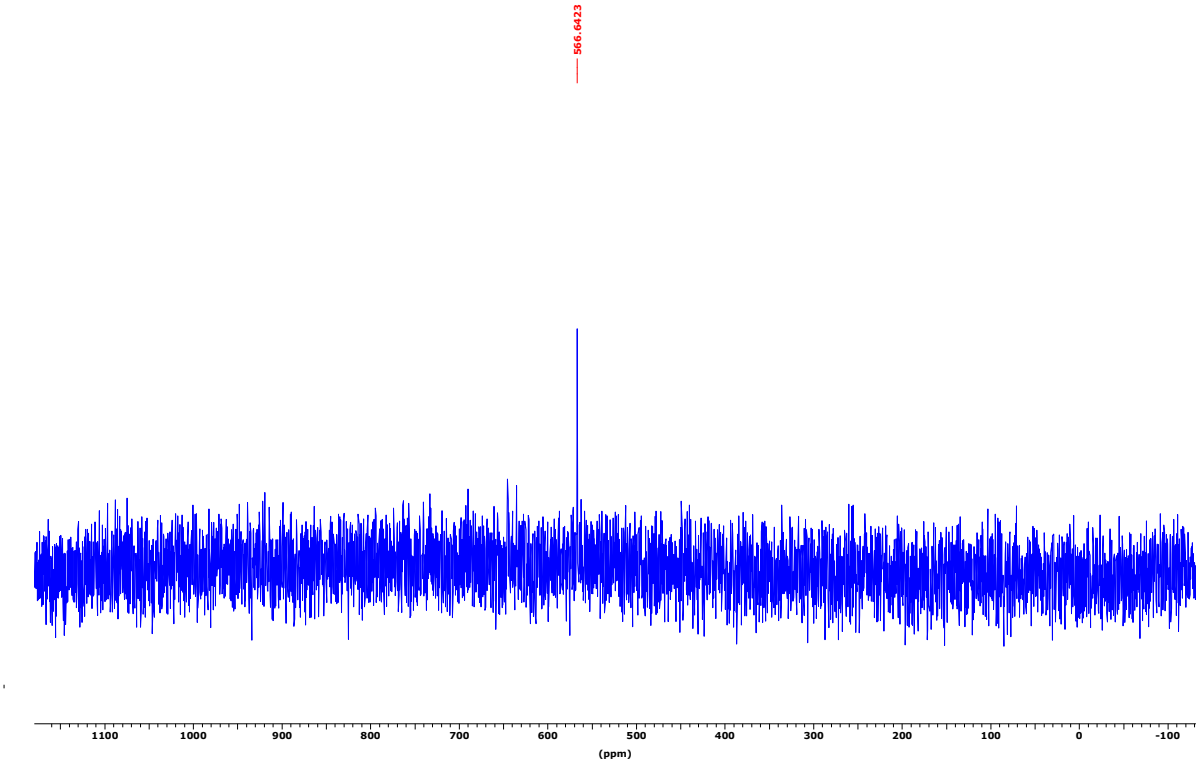

7.2676
3.5982
3.5466
1.1868
0.0000
Integral
12.000
17.997
(ppm)

4c

^{13}C


175.8912
158.2536
77.1600
42.3660
12.7853
(ppm)

^{77}Se



4. FTMS (ESI^+) isotopic pattern for selenacalix[3]triazine 2a and ESI-MS of the [2c–HSO_4^-] complex

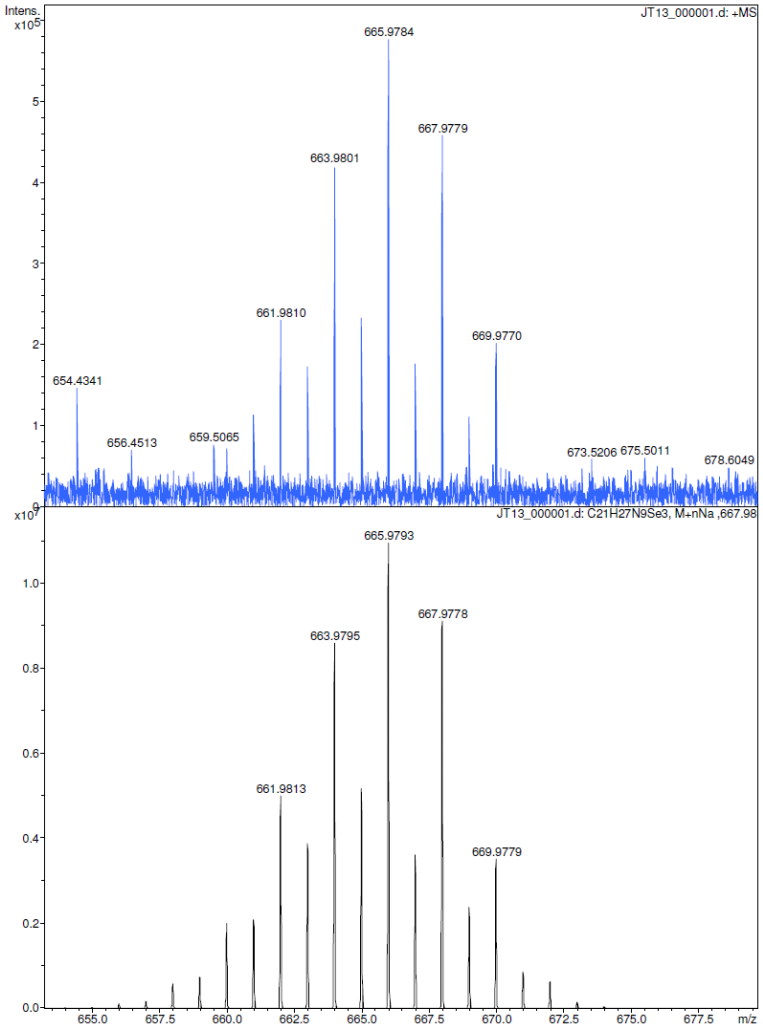


Figure S1 Observed (top) and theoretical (bottom) (high resolution) ESI-MS isotopic pattern for selenacalix[3]triazine **2a** ($[M+Na]^+$).

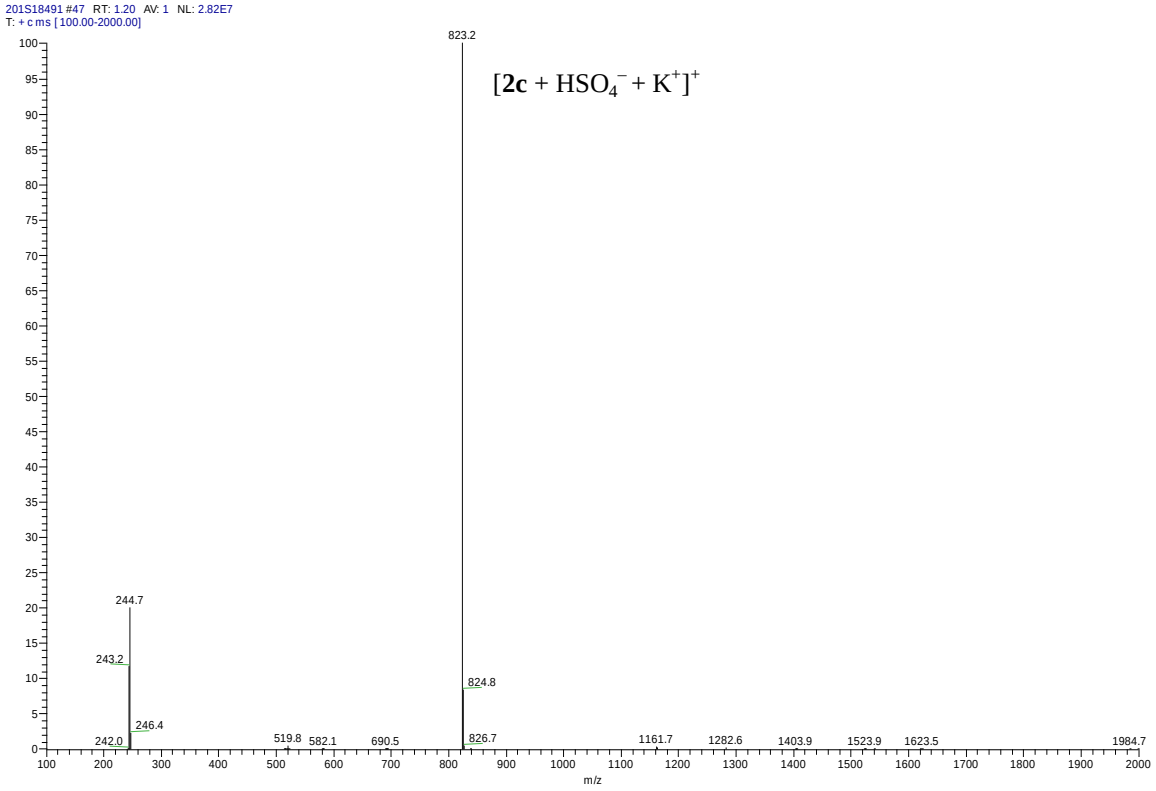


Figure S2 ESI-MS(+) spectrum for the complex of selenacalix[3]triazine **2c** and HSO_4^-.

5. X-ray crystallographic data and additional (packing) figures for selenacalix[3]triazines 2c, 3c and 4c

For the structures of compounds **2c**, **3c** and **4c** X-ray intensity data were collected on a SMART 6000 diffractometer equipped with a CCD detector using CuKα radiation (λ = 1.54178 Å), and using ϕ and ω scans. The images were interpreted and integrated with the program SAINT from Bruker.[8] Both structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[9] Nonhydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode and isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC 808717/808718/816095 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

*Crystal data for compound **2c***
$C_{23}H_{33}N_{13}Se_3$, M = 728.50, crystallization by slow evaporation of a CH_2Cl_2/CH_3CN (2:3) solution of **2c**, monoclinic, $P2_1/n$ (No. 14), a = 16.628(12), b = 10.688(5), c = 16.662(12) Å, β = 94.87(3)°, V = 2951(3) Å^3, T = 100(2) K, Z = 4, ρ_{calc} = 1.640 g cm^{-3}, μ(Cu-Kα) = 4.858 mm^{-1}, F(000) = 1456, crystal size 0.4 × 0.2 × 0.1 mm, 5511 independent reflections (R_{int} = 0.0574). Final R = 0.0388 for 4792 reflections with $I > 2\sigma(I)$ and *wR2* = 0.0933 for all data and a GoF (S) = 1.163. CCDC 808717

*Crystal data for compound **3c***
$C_{23}H_{33}Br_2CuN_{13}Se_3$, M = 951.85, crystallization by slow evaporation of a CH_2Cl_2/CH_3CN (1:1) solution of **3c**, monoclinic, $P2_1/c$ (No. 14), a = 11.0691(15), b = 24.187(3), c = 12.665(2) Å, β = 107.014(7)°, V = 3242.4(8) Å^3, T = 100(2) K, Z = 4, ρ_{calc} = 1.950 g cm^{-3}, μ(Cu-Kα) = 8.007 mm^{-1}, F(000) = 1852, crystal size 0.3 × 0.2 × 0.15 mm, 5637 independent reflections (R_{int} = 0.0916). Final R = 0.0850 for 4963 reflections with $I > 2\sigma(I)$ and *wR2* = 0.1855 for all data and a GoF (S) = 1.029. CCDC 808718

*Crystal data for compound **4c***
$C_{21}H_{30}BrCuN_{12}Se_3$, M = 830.90, crystallization by slow evaporation of a CH_2Cl_2/CH_3CN (1:1) solution of **5c**, rhombohedral, R-3c (No. 167), $a = b$ = 16.8242(2), c = 72.520(2) Å, V = 17777.0(6) Å^3, T = 293(2) K, Z = 24, ρ_{calc} = 1.863 g cm^{-3}, μ(Cu-Kα) = 7.122 mm^{-1}, F(000) = 9744, crystal size 0.3 × 0.15 × 0.05 mm, 3837 independent reflections (R_{int} = 0.0735). Final R = 0.0554 for 3309 reflections with $I > 2\sigma(I)$ and *wR2* = 0.1447 for all data and a GoF (S) = 1.069. CCDC 816095

8 SAINT, Manual Version 5/6.0, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, 1997.
9 SHELXTL-NT, Manual Version 5.1, Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, 1997.

For selenacalix[3]triazine **2c**, the macrocycles are stacked on top of each other, forming columns along the [010] direction (Figure S3). One of the linking Se atoms is perfectly stacked on top of the triazine unit of an underlying symmetry-equivalent molecule (3.42 Å distance to the triazine centroid). The two other Se atoms are not similarly stacking, because a MeCN solvent molecule is positioned between two symmetry-equivalent molecules, in addition stacking to an underlying triazine unit (N-centroid distance 3.27 Å). Consequently, pairs of molecules are arranged in a herringbone pattern along the crystallographic [100] direction (Figure S4).

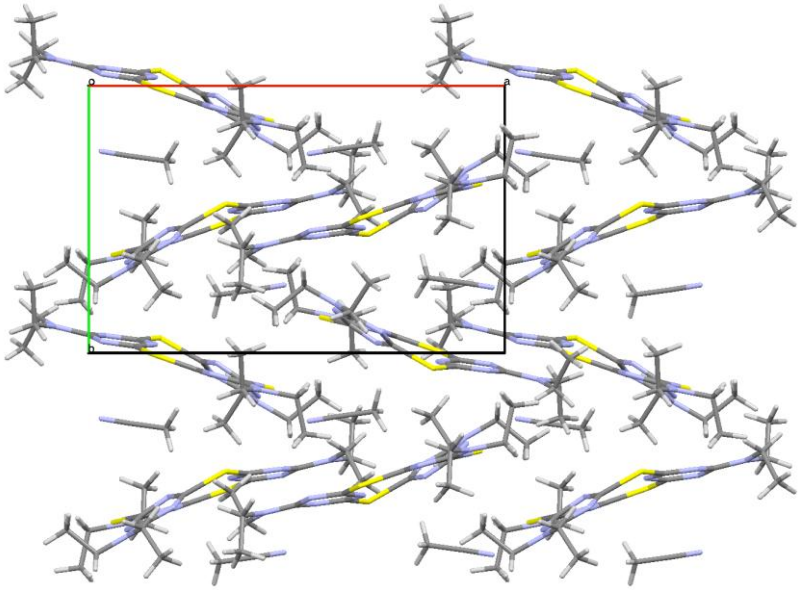


Figure S3 Packing of the crystal structure of selenacalix[3]arene **2c** (view along the *c* axis).

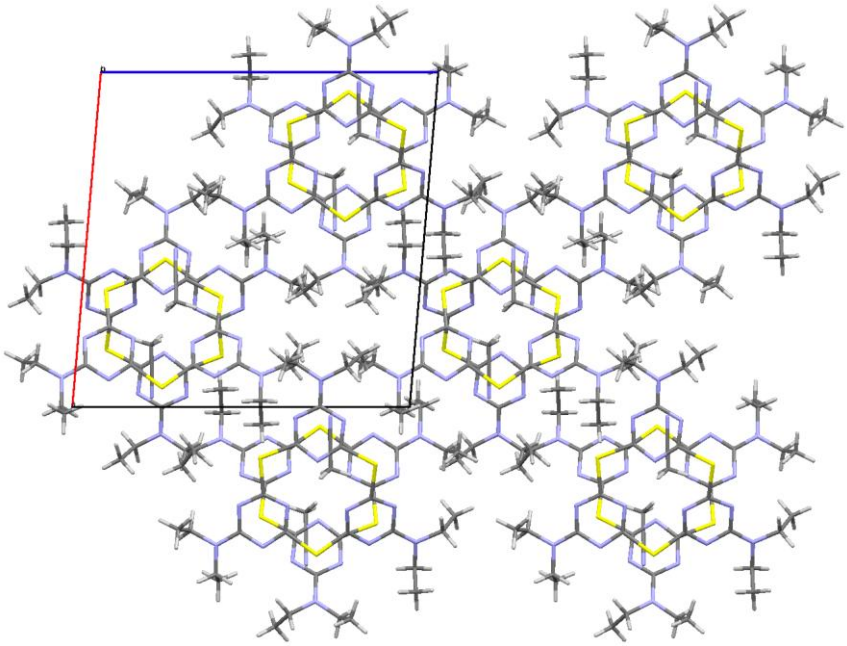


Figure S4 Packing of the crystal structure of **2c**, showing the formation of columns along the *b* axis.

In comparison with the structure of the free ligand **2c**, the Cu^{II} complex **3c** adopts a less planar conformation (inclination of the triazine rings: 12.4°, 12.4° and 14.1° with respect to the plane of the Se atoms). The Cu^{II} ion coordinates tridentately to the three interior triazine N atoms and the coordination environment is completed by the two Br^- anions. The Cu^{II} coordination sphere can be described as distorted square pyramidal with a τ value = 0.38. In the packing "dimers" of selenacalix[3]arene molecules are generated by two symmetry-equivalent molecules, related by a crystallographic inversion center (Figure S5). These two molecules perfectly stack on each other, *i.e.* the Se atoms of one macrocycle stack on the triazine rings of the inversion-related molecule and vice versa.

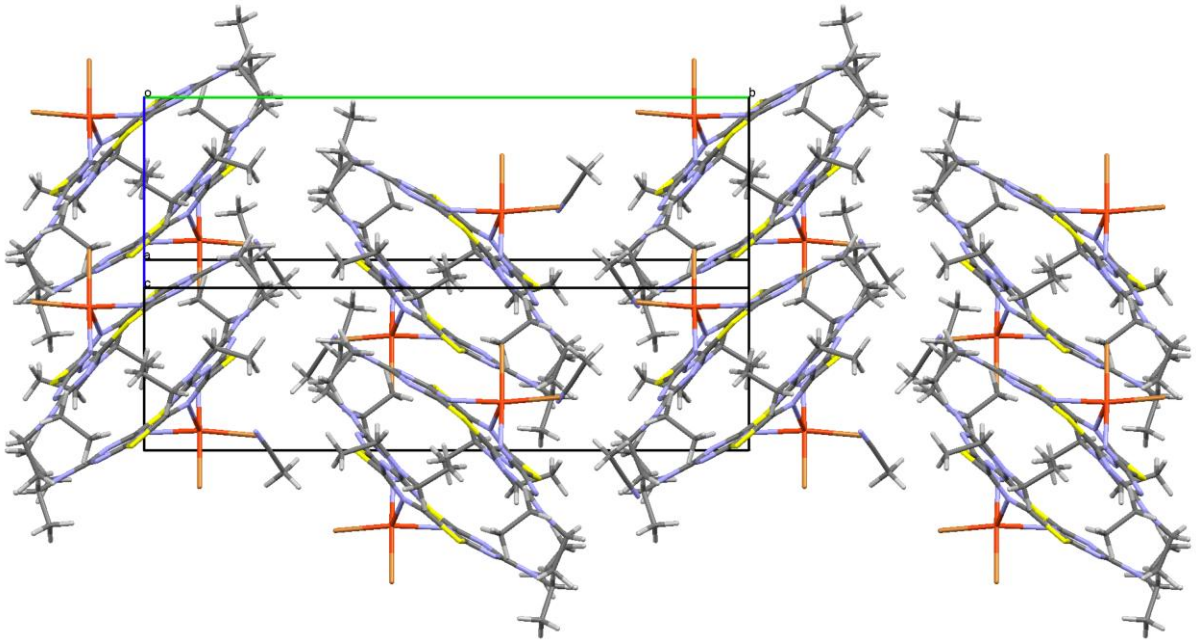


Figure S5 Packing of the crystal structure of Cu^{II} complex **3c**.

The asymmetric unit of the structure of Cu^{I} complex **4c** consists of two times one third of the total complex. By crystallographic symmetry two complete different molecules were generated (Figure S6). In comparison with the structure of the Cu^{II} compound **3c**, the selenacalix[3]triazine macrocycle adopts a less planar conformation. For the first molecule, the same inclination of 16.1° is observed for all three triazine rings with respect to the plane of the Se atoms, because of the rhombohedral crystal symmetry. For the second molecule, an inclination of 16.4° is observed. For both molecules, the Cu^{I} ion coordinates tridentately to the three interior triazine N atoms and the coordination environment is completed by one bromide anion. The Cu^{I} coordination sphere can be described as trigonal pyramidal, with the three interior triazine N atoms in the basal plane and the Br^{-} anion in the apical position.
In the packing, similar to the structure of the Cu^{II} complex, "dimers" of selenacalix[3]arene molecules are generated by crystallographic symmetry (Figure S7). The first and second molecule both form dimers with their own symmetry-equivalent molecules. In each dimer, the two molecules perfectly stack on each other, *i.e.* the Se atoms of one macrocycle stack on the triazine rings of the symmetry-related molecule and *vice versa* (distances of 3.75 Å and 3.85 Å between the Se atoms and the triazine ring centroids for the first and second dimer, respectively). The CuBr moiety is oriented outwards from the dimer.

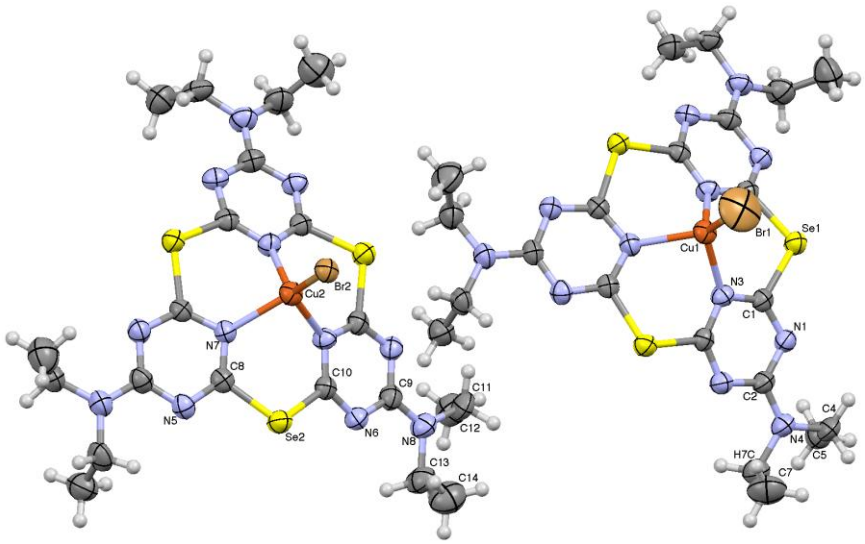


Figure S6 ORTEP representation (with atom labeling scheme) of Cu^{I} complex **4c**. Thermal displacement ellipsoids are shown at the 50% probability level.

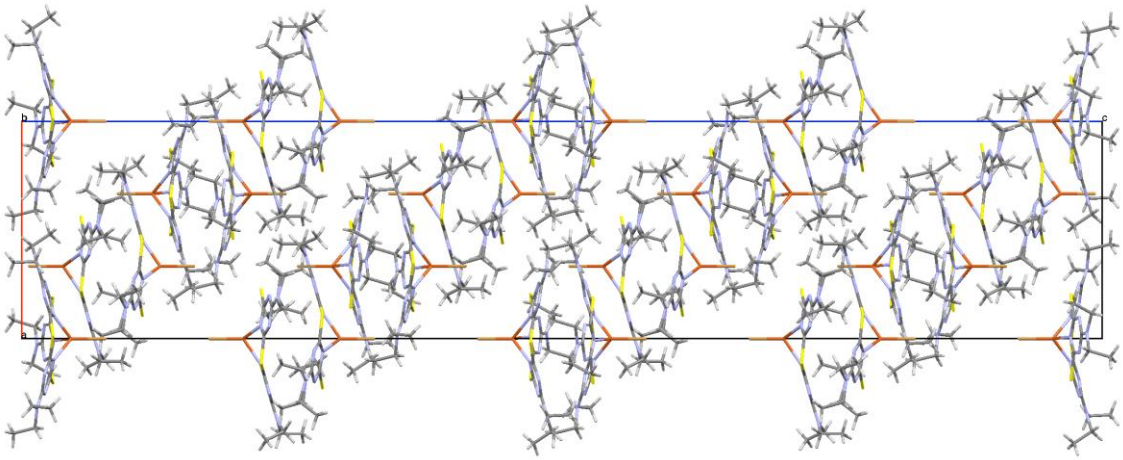


Figure S7 Packing of the crystal structure of Cu^{I} complex **4c**, showing the existence of dimers generated by two symmetry-equivalent molecules.

6. Additional data on the metal salt titrations and anion binding experiments

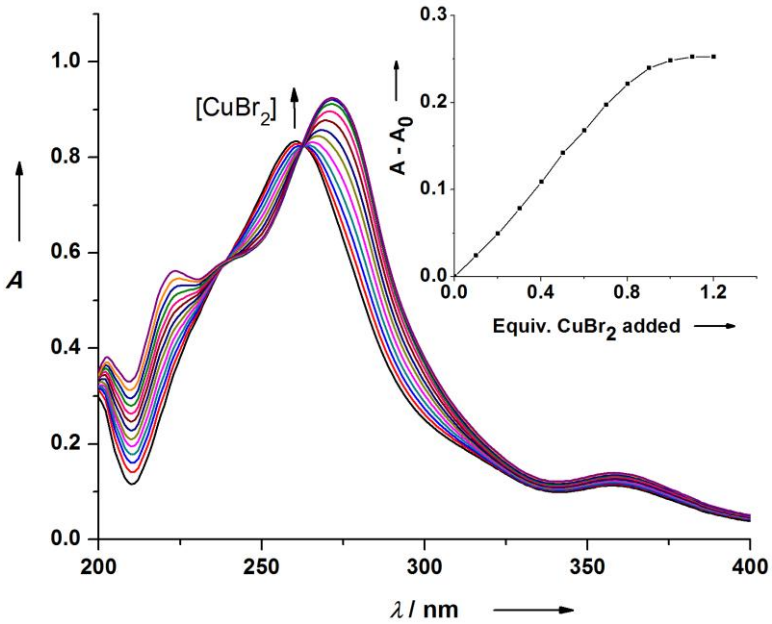


Figure S8 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with $CuBr_2$ (0, 0.11, 0.21, 0.32, 0.43, 0.53, 0.64, 0.75, 0.85, 0.95, 1.06, 1.16, 1.27, 1.59×10^{-5} M). Inset: variation of absorbance vs. equiv $CuBr_2$ added.

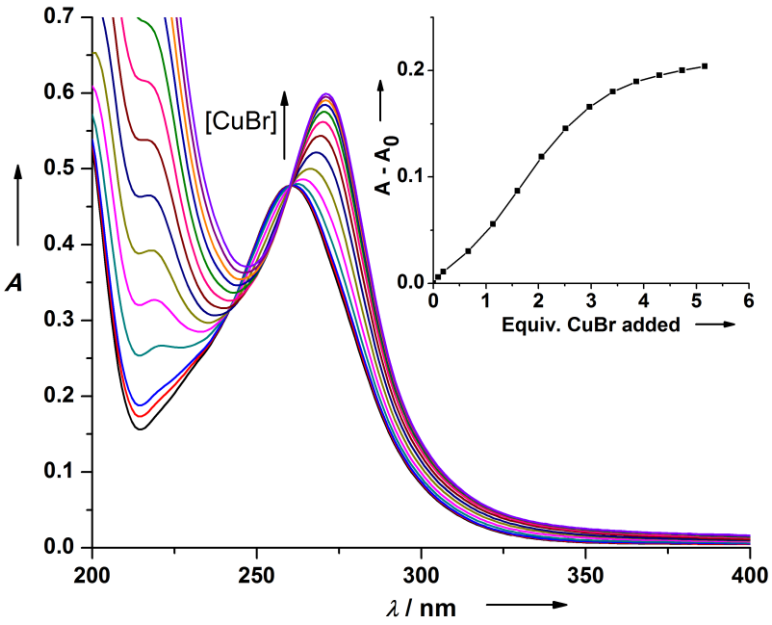


Figure S9 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with CuBr (0, 0.09, 0.19, 0.68, 1.15, 1.63, 2.10, 2.56, 3.02, 3.48, 3.93, 4.37, 4.81, 5.25×10^{-5} M). Inset: variation of absorbance vs. equiv CuBr added.

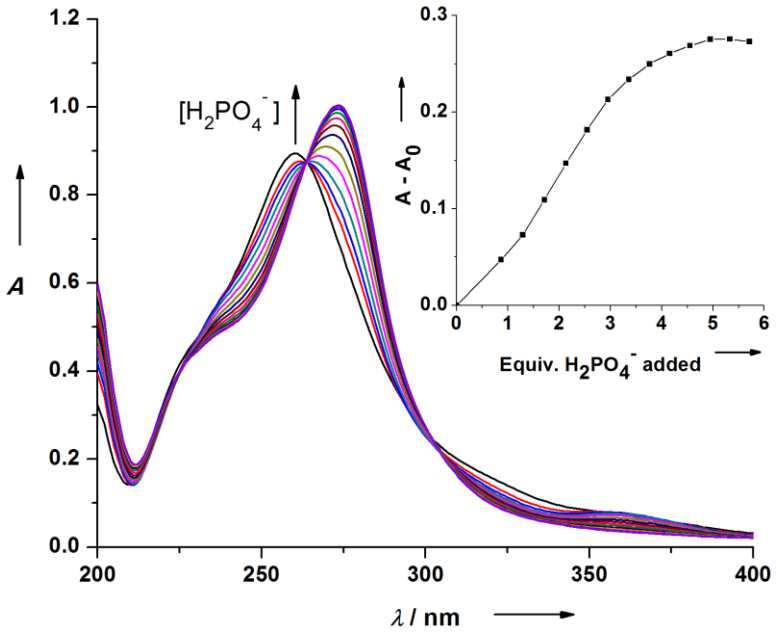


Figure S10 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with tetrabutylammonium dihydrogen phosphate (0, 0.91, 1.37, 1.82, 2.26, 2.70, 3.14, 3.57, 3.99, 4.41, 4.83, 5.25, 5.66, 6.07×10^{-5} M). Inset: variation of absorbance vs. equiv dihydrogen phosphate added.

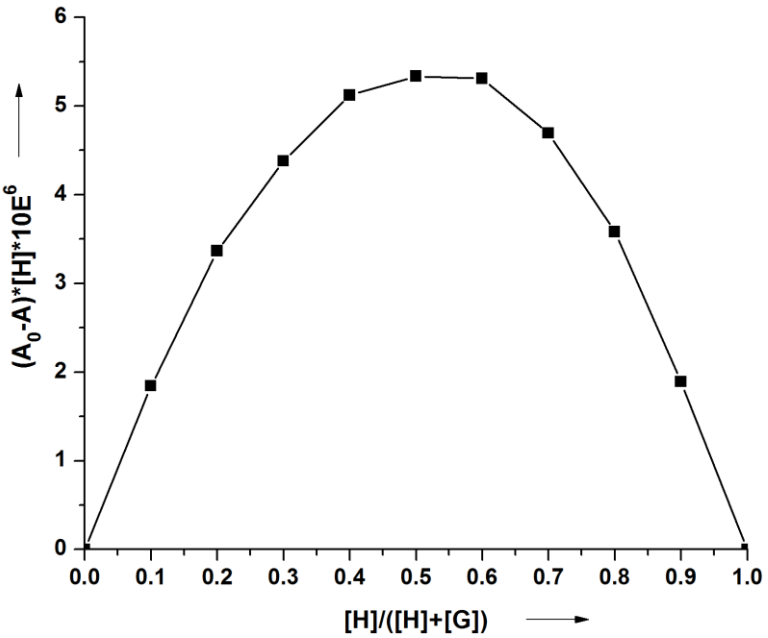


Figure S11 Job plot for the complexation of **2c** (2×10^{-5} M) with tetrabutylammonium dihydrogen phosphate in CH_3CN.

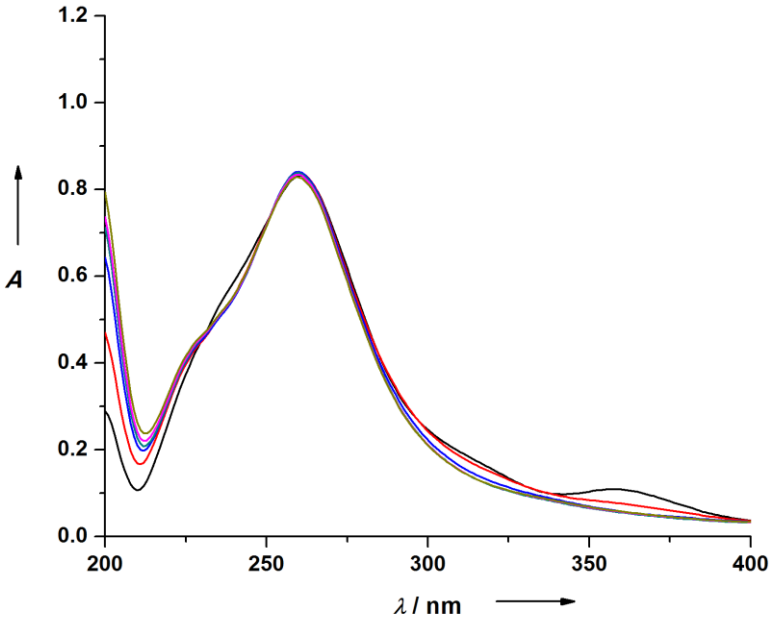


Figure S12 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with tetrabutylammonium bicarbonate (0, 3.21, 6.36, 9.44, 12.47, 12.35, 26.76, 37.29×10^{-5} M).

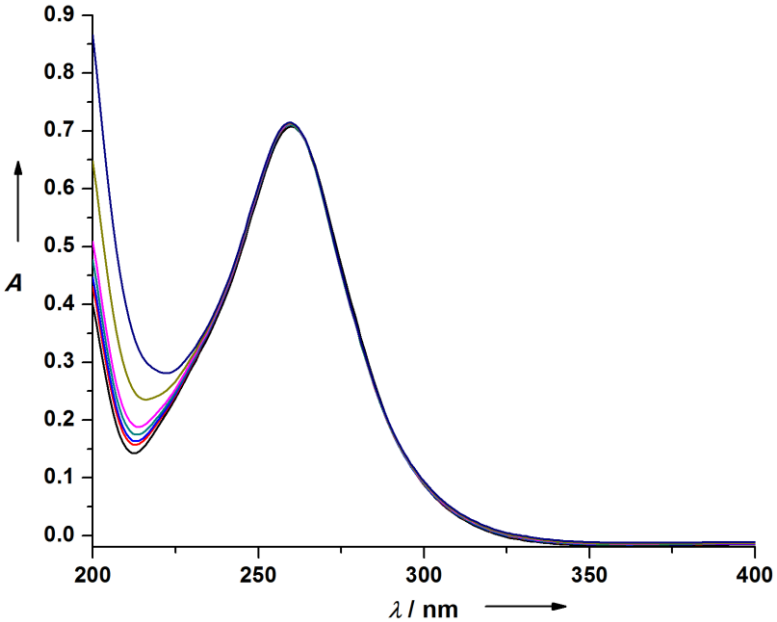


Figure S13 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with tetrabutylammonium acetate (0, 1.36, 2.70, 5.29, 9.00, 14.75, 24.82×10^{-5} M).

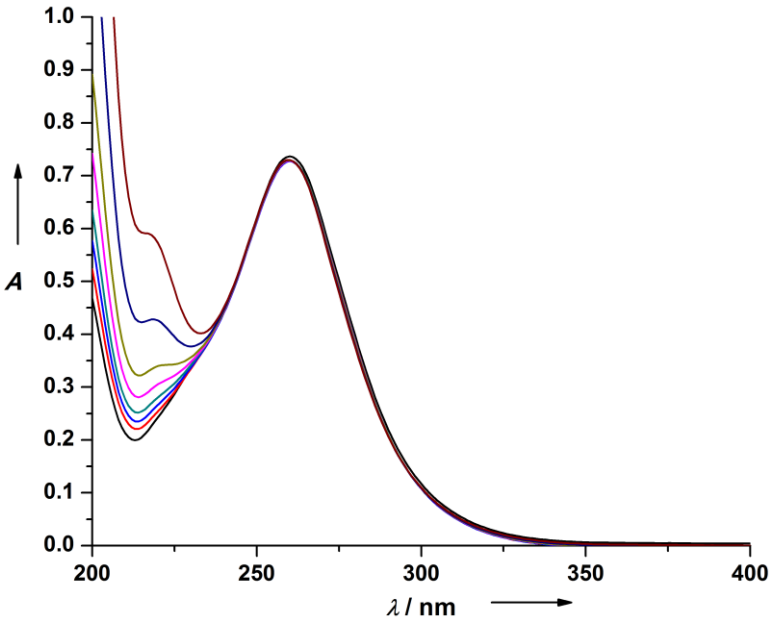


Figure S14 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with tetrabutylammonium chloride (0, 0.38, 1.14, 1.88, 3.33, 5.39, 8.59, 14.21×10^{-5} M).

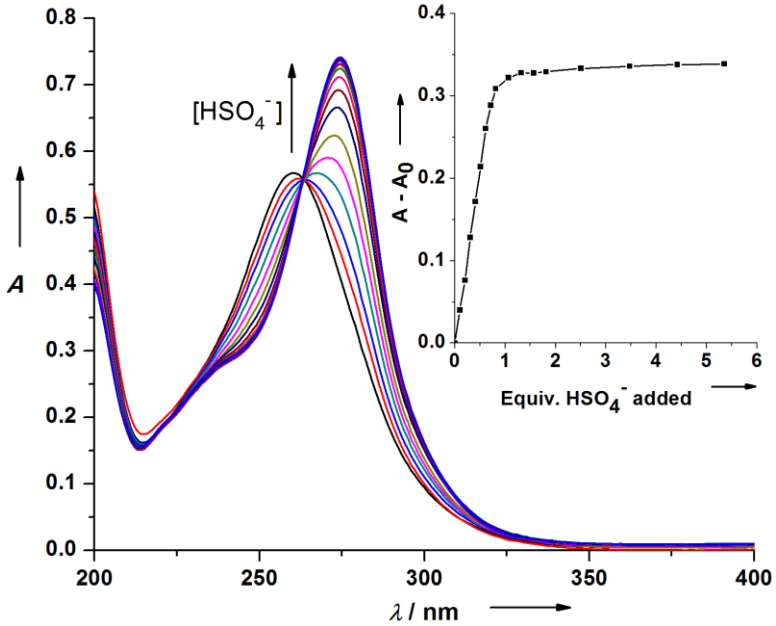


Figure S15 UV/Vis titration of **2c** (2 mL, 1×10^{-5} M in CH_3CN) with tetrabutylammonium hydrogen sulfate (0, 0.10, 0.21, 0.31, 0.42, 0.52, 0.62, 0.73, 0.83, 1.08, 1.34, 1.59, 1.85, 2.55, 3.53, 4.50, 5.45×10–5 M). Inset: variation of absorbance at λ = 275 nm vs. equiv HSO_4^- added.

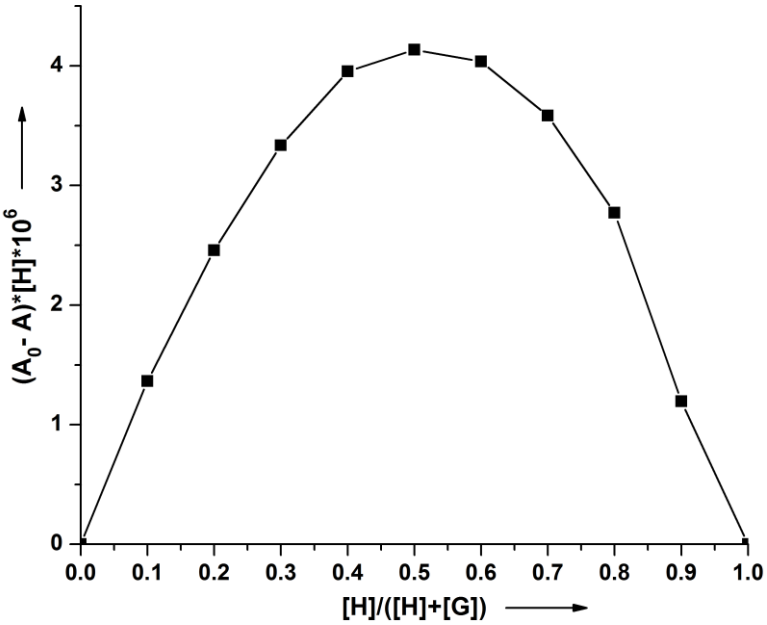


Figure S16 Job plot for the complexation of **2c** (2×10^{-5} M) with tetrabutylammonium hydrogen sulfate in CH_3CN.