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SUPPLEMENTARY INFORMATION

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Quantum superposition of molecules beyond 25 kDa

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Supplementary Information for

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Acronyms list:

- **DCTB:** *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile
- **DHB:** 2,5-Dihydroxybenzoic acid
- **DMF:** *N*,*N*-dimethylformamide
- **HR-MALDI-TOF:** High resolution matrix assisted laser desorption/ionization time of flight mass spectrometry
- **HRMS:** High resolution mass spectrometry
- **NMR:** Nuclear magnetic resonance spectroscopy
- **TCNQ:** Tetracyanoquinodimethane
- **TLC:** Thin Layer Chromatography
- **UV/VIS:** Ultraviolet-to-visible absorption spectroscopy

Supplementary Methods

General Remarks

Reagents and solvents: All commercially available compounds were purchased from Sigma-Aldrich, Acros, Apollo Scientific, Alfa Aesar, and Fluorochem and were used without further purification unless otherwise stated.

Analytics and instruments: Size exclusion column chromatography was performed using Bio Beads^{TM} SX-3 from Bio Rad in toluene in a glass column with a diameter of 5.5 cm and a height of 38 cm. The solvent was technical grade. TLC was performed with silica gel 60 F254 glass plates purchased from Merck. NMR experiments were performed on Bruker Avance III NMR spectrometers operating at 250 MHz proton and 235 MHz fluorine frequencies. The instrument was equipped with a direct-observe 5 mm BBFO smart probe and an actively shielded z-gradient (10 A). The chemical shifts are reported in ppm relative to the residual $CDCl_3$ peak and the J values are given in Hz (± 0.1 Hz). Standard Bruker pulse sequences were used, and the data was processed on Topspin 3.2 (Bruker). MALDI-TOF mass spectra were recorded on a Bruker rapifleX LRF spectrometer using tetracyanoquinodimethane (TCNQ) as the matrix. High resolution mass spectra (HRMS) were measured on a Bruker solariX spectrometer with a MALDI source and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. UV/VIS absorption spectra were recorded on a Jasco V-770 Spectrophotometer.

Synthesis of the target molecular library beyond 25 kDa

Compound 1: A solution of [5-bromo-10,15,20-tris(perfluorophenyl)porphyrinato] zinc(II)(**3**)[32] (200 mg, 210 µmol, 4.0 eq), (methanetetrayltetrakis(benzene-4,1-diyl))tetraboronic acid(**2**)[33] (26.0 mg, 52.5 µmol, 1.0 eq) and $NaHCO_3$ (44.1 mg, 525 µmol, 10 eq.) in THF:H_2O (9:1, 10 mL) was purged with argon for 20 minutes. $Pd(PPh_3)_4$ (6.07 mg,

5.25 µmol, 0.1 eq.) was added and the reaction mixture was placed in a pre-heated oil bath for 2 hours while stirring. The reaction mixture was allowed to cool down to room temperature, filtered over a plug of silica eluted with CH_2Cl_2 and concentrated under reduced pressure. The crude product was dissolved in toluene and subjected to size-exclusion column chromatography to yield the target compound **1** (174 mg, 45.6 mmol, 87%) as a microcrystalline bright purple solid. **TLC** (SiO_2, CH_2Cl_2/cyclohexane (1:1)): R_f = 0.25. **UV/VIS (CH_2Cl_2):** λ_{max} [nm] = 418, 540, 581. **^{1}H-NMR** (250 MHz, $CDCl_3$, 298 K, δ/ppm): 9.41 (d, $^3J_{HH}$ = 4.8 Hz, 2H, H_β), 8.99 (“s”, 6H, H_β), 8.65 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H_{Ph}), 8.52 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H_{Ph}). **^{19}F NMR** (235 MHz, $CDCl_3$, 298 K, δ/ppm): -136.58 – -137.29 (m), -151.66 – -152.99 (m), -161.55 – -162.41 (m). **HR-MALDI-TOF** *m/z* = 3793.0542 ($[M+H]^+$ requires 3793.0528). The error of -0.4 ppm is within the acceptable range for HRMS.

Target Library 1*L*: 1*H*,1*H*,2*H*,2*H*-perfluorodecanthiol (4.52 mL, 15.8 mmol, 500 eq.) was added to a degassed solution of compound **1** (120 mg, 31.6 µmol, 1.0 eq) and freshly dried Cs_2CO_3 (5.15 g, 15.8 mmol, 500 eq) in dry and degassed DMF (4.52 mL). The mixture was stirred for 15 minutes at room temperature under argon atmosphere. The product precipitated from the mixture and *Fluorinert FC-72* was added. The mixture was successively washed with water, the organic phase was separated, dried over anhydrous Na_2SO_4 and was concentrated under reduced pressure yielding the target Library 1*L* (902 mg) as an amorphous dark purple solid which was characterized by MALDI-ToF mass spectrometry. It is this library that is used in the interference experiments described in the main text.
UV/VIS (*Fluorinert FC-72*): λ_{max} [nm] = 442, 570, 620. **MALDI-TOF** *m/z* (rel. intensity [%]) [number of substitutions] = 25390 (40) [47], 25853 (72) [48], 26312 (88) [49], 26777 (100) [50], 27239 (62) [51], 27703 (35) [52].

Supplementary Figure 1: *Synthetic route to the target library* ***1L****. A four-fold Suzuki-Miyaura cross-coupling reaction of compounds* ***3***[32] *and* ***2***[33] *yields the tetrameric porphyrin intermediate compound* ***1****, which yields the desired library* ***1L*** *following fluoroalkylsulfanyl functionalization, in which R = F is replaced by R =* $C_{10}H_4F_{17}S$ *in up to 60 possible sites (see Figure 1).*

Supplementary Figure 2: *QMF mass spectra characterization.* ***a)*** *QMF mass spectra from the quadrupole at LUMI showing the shift to higher mass and narrowing of the mass peak as the resolution is improved. This data shows that with a 30% detector resolution and a 21 kDa setpoint, we would only observe the mass library centered at 27 kDa and not fragments at 15 kDa and below. The absolute calibration is scaled to agree with the MALDI-TOF spectra in Figure 3.* ***b)*** *QMF mass spectra as a function of electron impact energy in eV. The reduction of a secondary mass peak with electron energy shows that these fragments are born in the detector rather than the source. This secondary peak corresponds to dissociation of the molecule into two at the phenylmethane core.*

Supplementary Figure 3: *Influence of the LUMI laser desorption on the mass distribution. The filled blue peaks show a MALDI-TOF spectrum of the molecular library as recorded after synthesis. To characterize the effect of the LUMI desorption process on the mass distribution, material was collected about 30 cm behind the desorption source and then analyzed in the same MALDI-TOF setup as the pure library. This post-desorbed spectrum is shown by the red unfilled peaks and shows that the distribution remains largely unaffected. A small uncertainty remains regarding the exact level of fragmentation due to the possibility of macroscopic pieces of intact material being ejected along with the molecular beam, potentially contaminating the post-desorbed sample.*

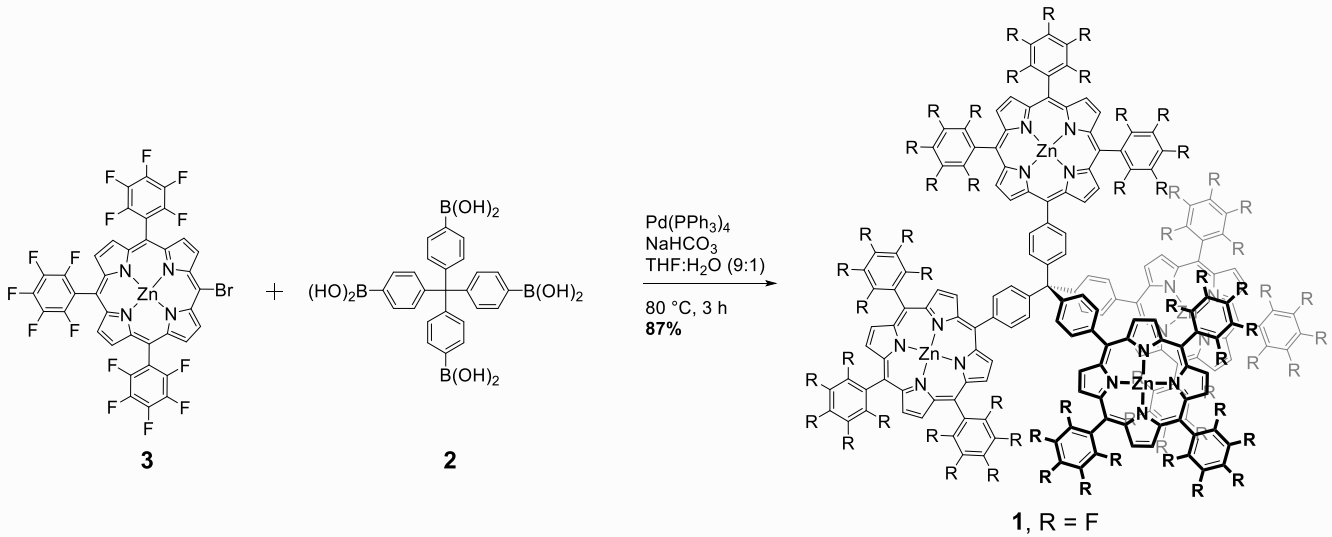
Supplementary Figure 4: *UV/VIS spectra of the oligoporphyrins. UV/VIS spectrum of ZnTPP in toluene (lower blue line) is compared to the tetrameric porphyrin intermediate in* CH_2Cl_2

(red line) and the functionalized oligoporphyrins in Fluorinert™ FC-72 (yellow line). The porphyrin spectra are scaled to agree with four times the value of the Soret band of ZnTPP. The red shift of the functionalized oligoporphyrins is attributed to the presence of the fluoroalkylsulfanyl chains.

Supplementary Figure 5: *Reference measurement procedure. Interference at LUMI is expected to produce fringes of the same periodicity as the gratings, 266 nm. To eliminate the contributions of source-based fluctuations in the interference data, the diffraction laser was modulated and data divided into laser-on and laser-off bins. Fourier transforms of the laser-on bins (blue), laser-off bins (red), and the ratio of on-to-off (yellow), shows that the strong 266 nm component (dashed vertical line) appears only when the diffraction laser is on. The diffraction laser was set to 1 W for these measurements.*

Supplementary Figure 6: *^{1}H-NMR spectrum of compound **1**. The typical signals of porphyrin beta protons and the AB system of the inner tetraphenylmethane core are characteristic for the product and confirm the successful preparation of the fully fluorinated oligoporphyrin intermediate compound, as shown in Supplementary Fig. 1.*

Supplementary Figure 7: *^{19}F-NMR spectrum of compound **1**. The three different fluorine resonances arise due to the difference in the chemical environment for either ortho, meta, or para connection with respect to the porphyrin. The multiplicity of each of these resonances is given by the nuclei coupling of neighbouring fluorine atoms and additional minor diversity in the chemical environment due to the relative positions of the pentafluoro benzenes with respect to the tetraphenylmethane core.*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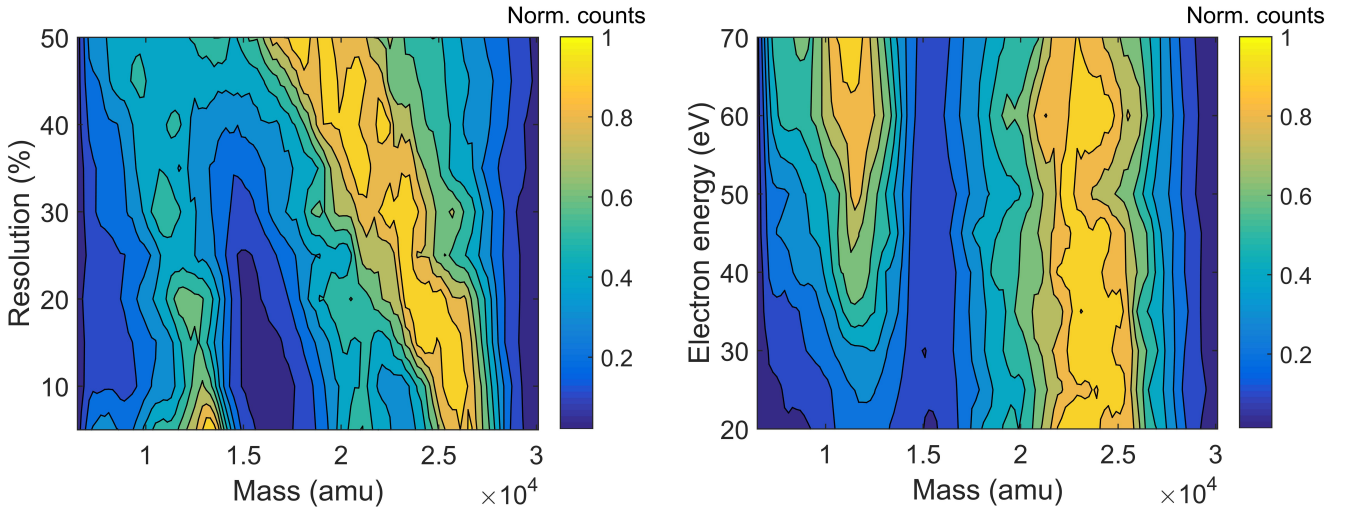
3
2
1, R = F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0.4
0.2
Resolution (%)
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40
30
20
10
1
1.5
2
2.5
3
Mass (amu)
×10^4
Norm. counts
1
0.8
0.6
0.4
0.2
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50
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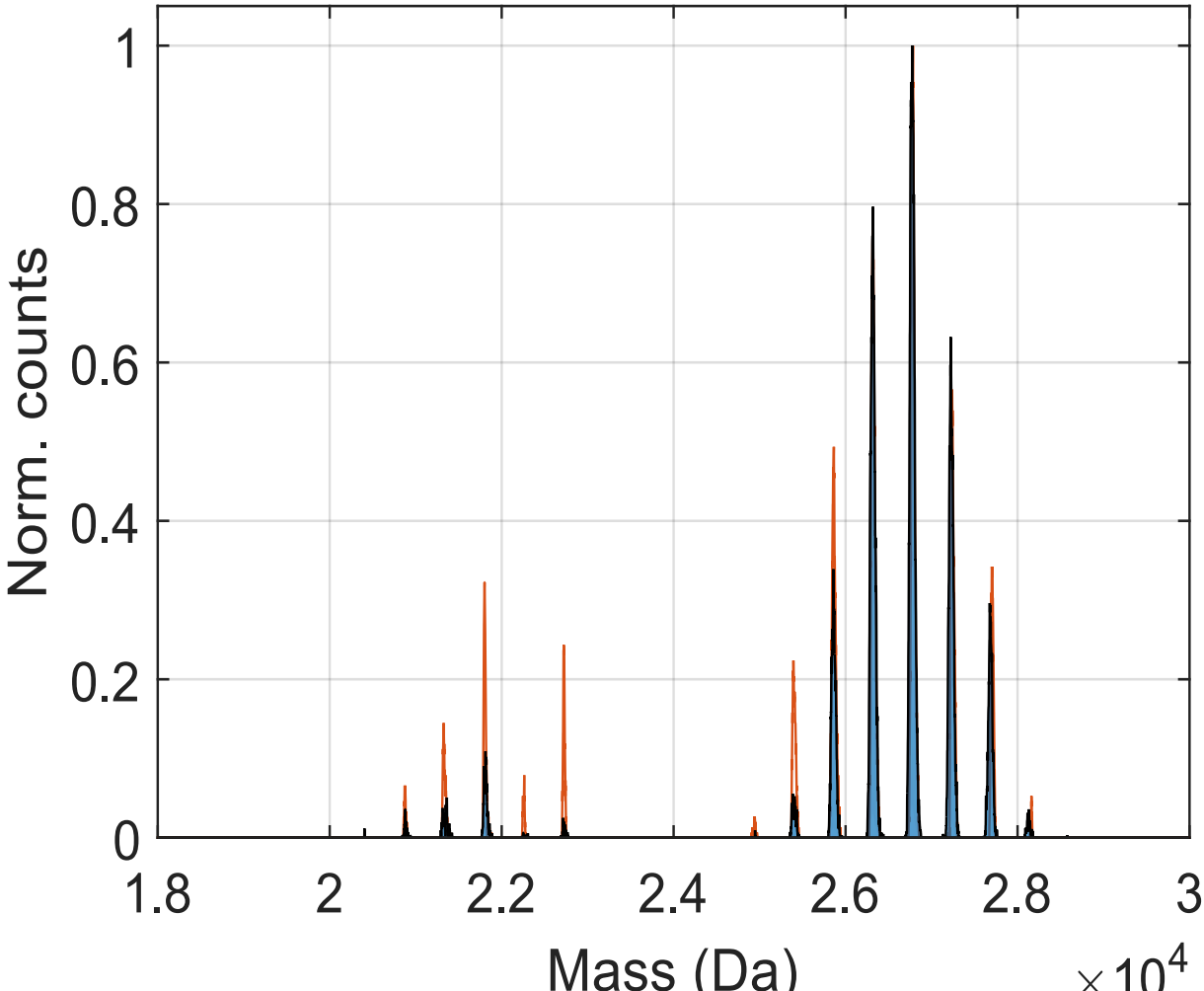
30
20
1
1.5
2
2.5
3
Mass (amu)
×10^4


Norm. counts
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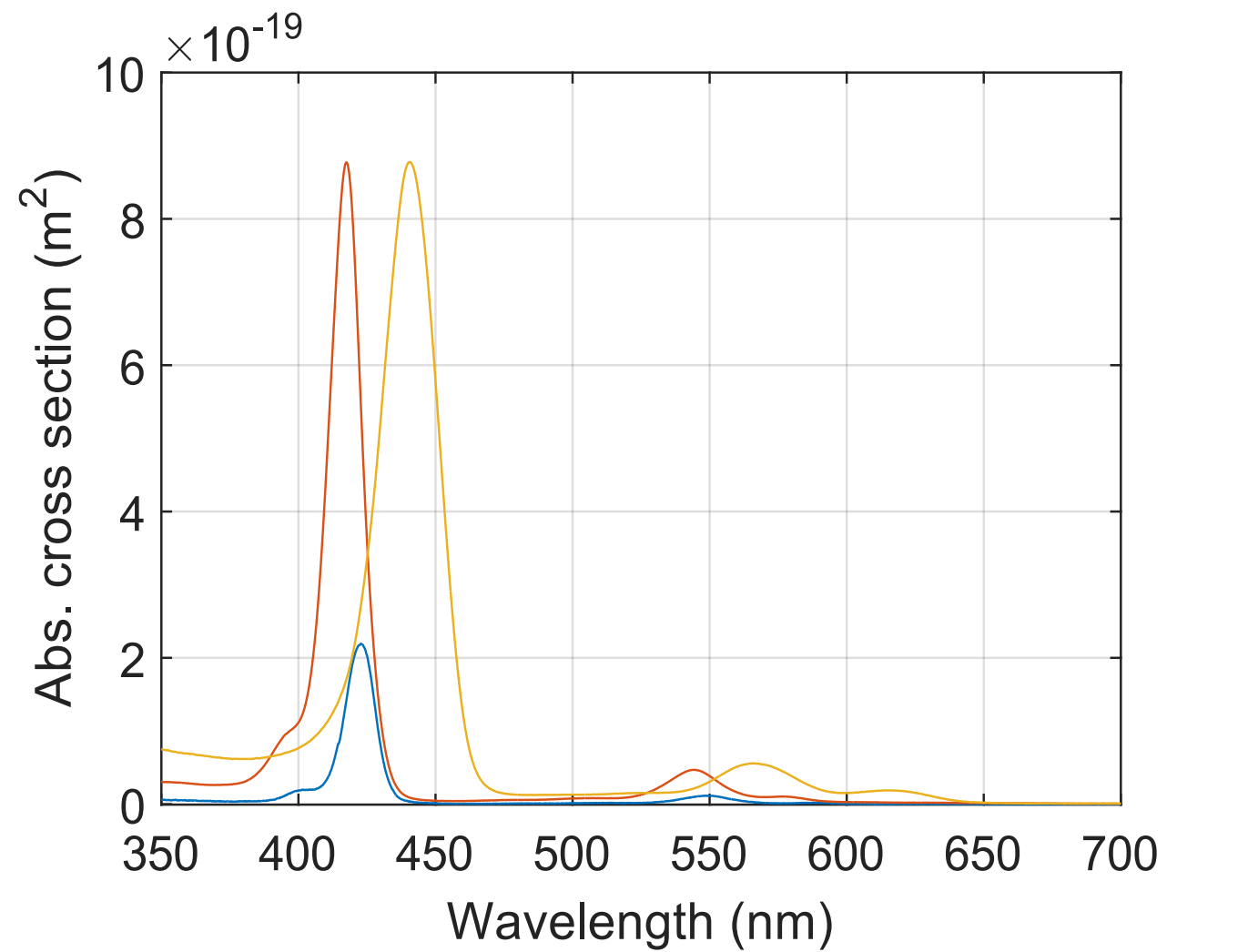
Mass (Da)
×10^4


×10^-19
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6
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2
0
Abs. cross section (m^2)
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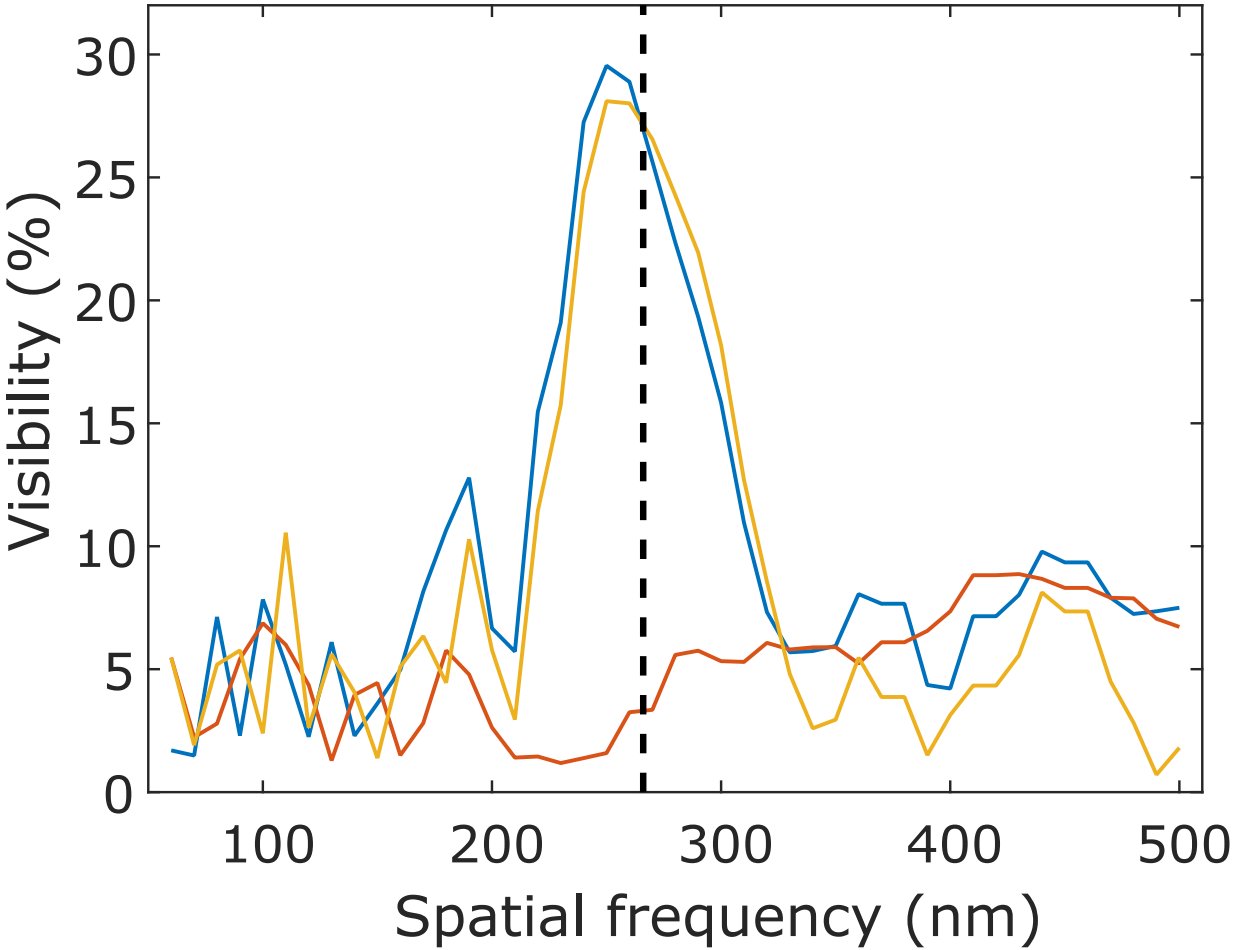
400
450
500
550
600
650
700
Wavelength (nm)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25
20
15
10
5
0
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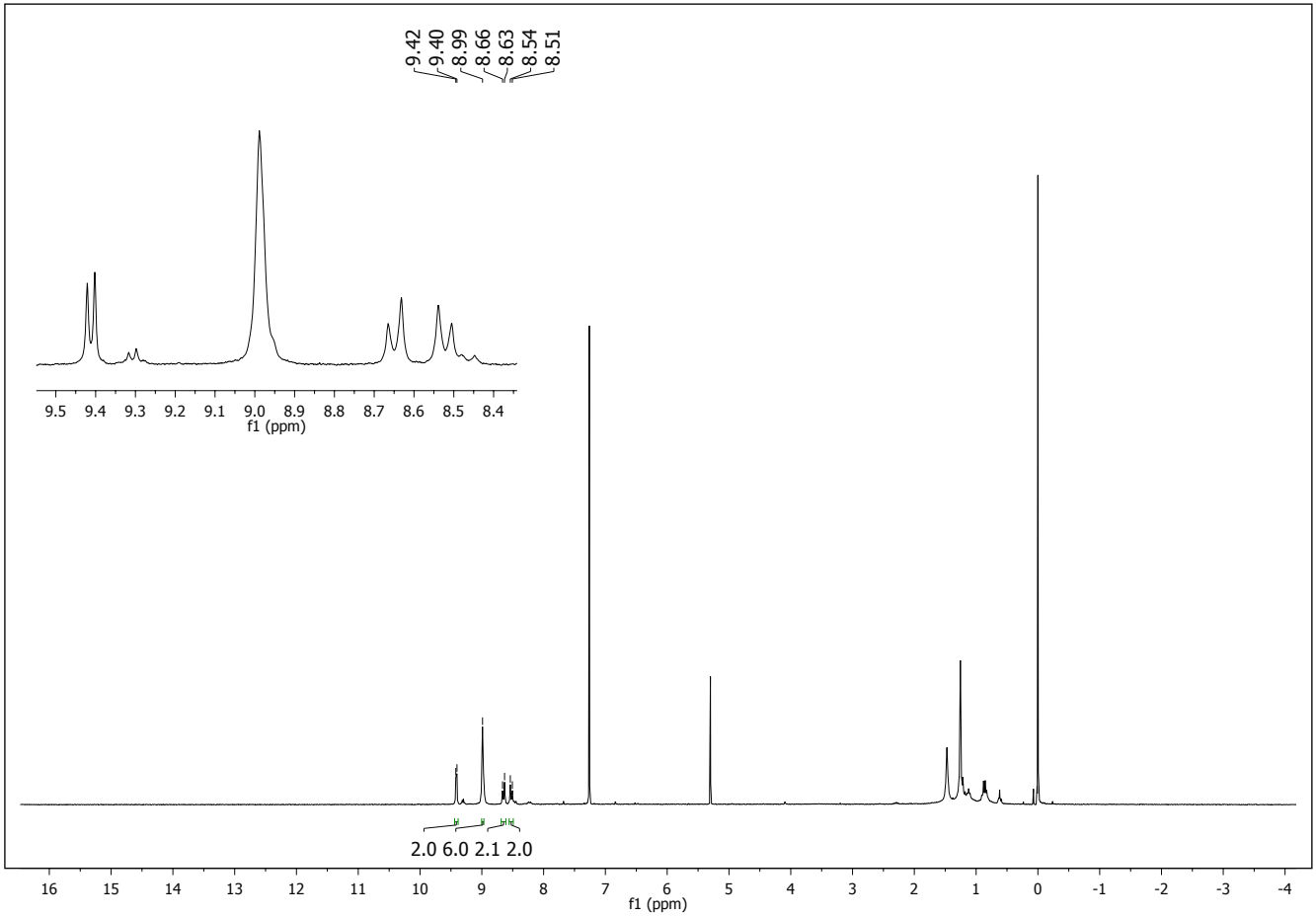
200
300
400
500
Spatial frequency (nm)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8.99
8.66
8.63
8.54
8.51
9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4
f1 (ppm)
2.0 6.0 2.1 2.0
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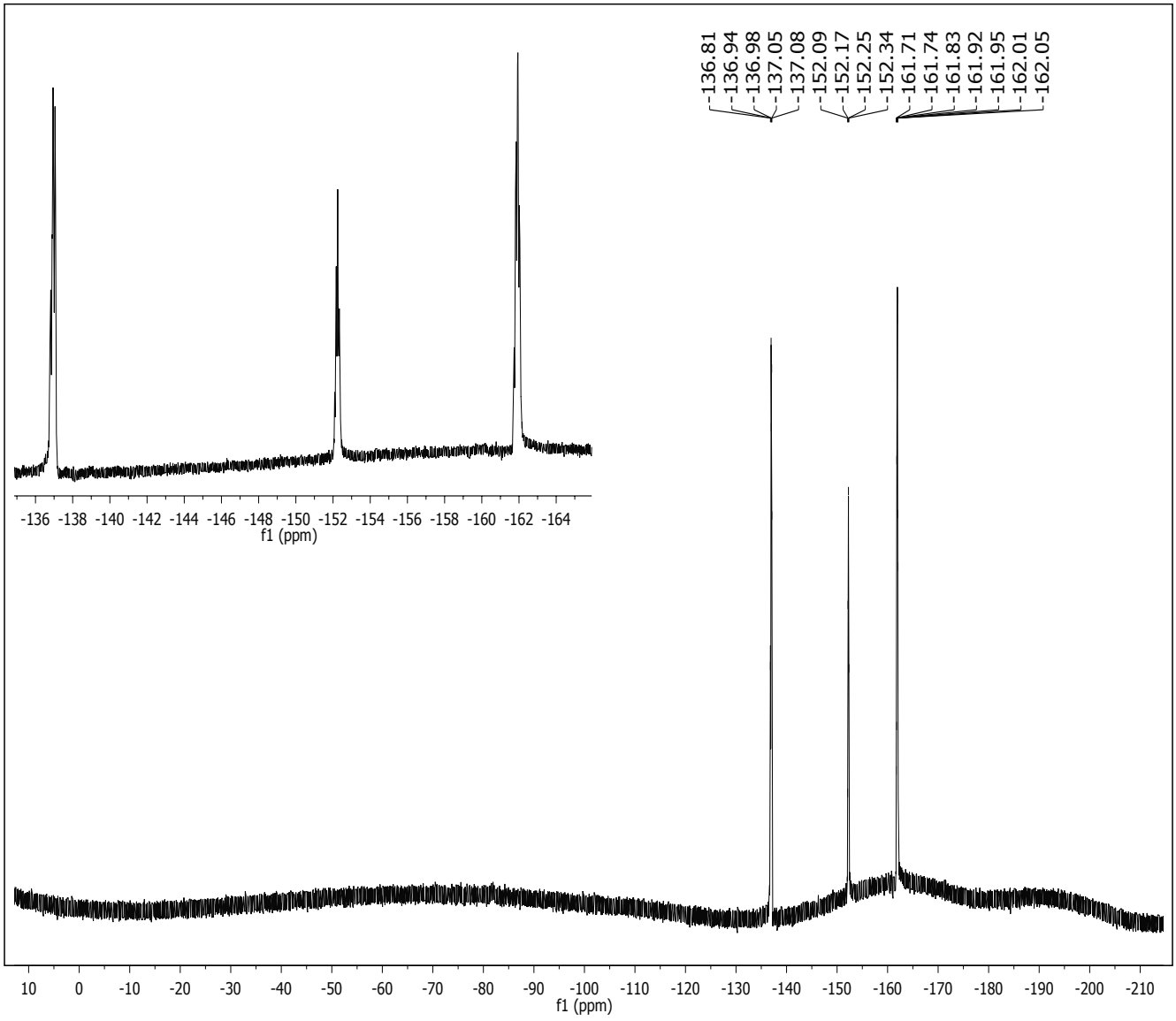
f1 (ppm)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136.98
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137.08
152.09
152.17
152.25
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161.71
161.74
161.83
161.92
161.95
162.01
162.05
-136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162 -164
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)