Atomically precise organomimetic cluster nanomolecules assembled via perfluoroaryl-thiol \textit{SnAr} chemistry

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Experimental Section

General considerations. Microwave synthesis reactions and all post-microwave work-up and characterization were performed under ambient conditions. For the purposes of this manuscript, “ambient conditions” refer to room temperature (20 - 28 °C) and uncontrolled laboratory air.

Materials. Deuterated solvents were purchased from Cambridge Isotope Laboratories. MilliQ water described in this manuscript refers to purified potable water with a resistivity at 25 °C of ≤18.2 MΩ⋅cm. [NEt₃H][B₁₂H₁₂] was purchased from Boron Specialties. EtOH (200 proof) was purchased from Decon Labs. Fmoc-L-amino acids (>98.5%) were purchased from Chem-Impex International, Inc. Piperidine (99%) was purchased from Spectrum. CaCl₂⋅2 H₂O (≥99%), MgCl₂⋅6 H₂O (≥99%), MnCl₂⋅4 H₂O (≥98%), diethyl ether (anhydrous, ≥99.9%), glycine (98%), and Gibco minimum essential medium were purchased from Fisher Scientific. Thiophenol (99%) and poly(ethylene glycol) methyl ether (average MW 750 Da, MW range 715 – 785 Da) were purchased from Acros Organics. HBS-P pH 7.4 buffer (10 mM HEPES, 0.005% v/v Tween P20) and 1 M ethanolamine-HCl (pH 8.5) were purchased from GE Healthcare Life Sciences. Fetal bovine serum was purchased from Sciencell Research Laboratories. FeCl₃⋅6 H₂O (≥97%), CsOH⋅1 H₂O (≥99.5%), H₂O₂ (30% in H₂O), [NⁿBu₄]OH (40% in H₂O), trifluoroacetic acid (TFA, 99%), triisopropysilane (98%), N,N-dimethylformamide (DMF, ≥99.8%; anhydrous, 99.8%), MeCN (≥99.9%), CH₂Cl₂ (≥99.5%), ethyl acetate (≥99.5%), hexanes (≥98.5%), MeOH (≥99.8%), N,N-diisopropylethylamine (≥99%), tetrabutylammonium hexafluorophosphate (≥99.0%, electrochemical grade), 1,2-ethanedithiol (≥98%), 1-hexanethiol (95%), benzyl mercaptan (99%), cysteamine (95%), 2-mercaptoethanol (≥99%), 1-thioglycerol (≥97%), O-(2-mercaptoethyl)-O’-methyl-hexa(ethylene glycol) (average Mₙ 356.48 Da, ≥95%), O-(2-mercaptoethyl)-O’-methylpolyethylene glycol (average Mₘ 2,000 Da), 1-thio-β-D-glucose tetraacetate (97%), N-
(tert-Butoxycarbonyl)-L-cysteine methyl ester (97%), isopropoxytrimethylsilane (98%), K₃PO₄ (≥98%), K₂CO₃ (≥99%), Tris (≥99%), and triethylamine (≥99%) were purchased from Sigma-Aldrich. All reagents were used as received unless otherwise indicated.

**Instruments.** Bruker AV300, AV400, AV500, and DRX500 spectrometers were used to obtain ¹H, ¹¹B, ¹³C{¹H}, and ¹⁹F NMR spectra and Bruker Topspin software was used to process the NMR data. ¹H and ¹³C{¹H} NMR spectra were referenced to residual solvent resonances in deuterated solvents (due to high humidity, H₂O resonances are often present). ¹¹B and ¹⁹F NMR spectra were referenced to BF₃·Et₂O and CFCl₃ external standards, respectively, at δ 0.0. *in situ* ¹¹B and ¹⁹F NMR spectroscopy was run unlocked and unshimmed. ¹¹B NMR spectra were baseline-corrected using the cubic spline correction tool within the Bruker Topspin software. Mass spectrometry data were acquired using a Thermo Scientific Q-Exactive Plus instrument with a quadrupole mass filter and Orbitrap mass analyzer or a Waters LCT Premier TOF system with ACQUITY LC and autosampler. IR spectroscopy was acquired on solid samples using a PerkinElmer Spectrum Two FT-IR spectrometer equipped with a diamond universal ATR probe. High resolution transmission electron microscopy (HRTEM) images were acquired with a FEI Titan electron microscope operating at 300 kV. Size exclusion chromatography-multi angle light scattering (SEC-MALS) was conducted on a GE AKTA PURE chromatographic system equipped with a WYATT miniDawn Treos MALS, WYATT optilab T-rEX RI detector, one Tosoh PWXL guard column (6.0 mm ID x 4.0 cm, 12 μm), and one Tosoh G4000PWxl (7.8 mm ID x 30 cm, 10 μm) column. Surface plasmon resonance (SPR) experiments were run on a GE Healthcare Life Sciences Biacore T100 instrument. Purification of peptides was done using a Waters HPLC system equipped with a UV/Vis detector set at λ = 214 nm.
**2D diffusion-ordered (DOSY) $^1$H NMR spectroscopy.** 2D DOSY experiments on purified samples of PEGylated OCNs were performed in D$_2$O at 30 °C on a Bruker AV 300 spectrometer. The data were processed with the standard Bruker Topspin software – the T1/T2 vargrad fitting function was used to determine the diffusion coefficients. 2D DOSY plots were created with the Bruker Topspin software. Hydrodynamic diameters were estimated based on the diffusion coefficients using the Stokes-Einstein Equation.

**High resolution transmission electron microscopy (HRTEM).** HRTEM samples were prepared by dropping 5 μL of 25 μg/mL aqueous sample solutions onto carbon copper grids (Ted Pella). The samples were then blotted once with a filter paper and then left to air-dry for 10 minutes. Then, 3 μL of a 2% w/w uranyl acetate aqueous solution was dropped on the grids, and subsequently blotted after 2 minutes.

**Size exclusion chromatography-multi angle light scattering (SEC-MALS).** Samples for SEC-MALS were prepared by dissolving sample in MilliQ water and filtering sample through a 0.20 μm PTFE Fisherbrand syringe filter. Eluent was Millipore filtered MilliQ water with 0.02% NaN$_3$ at 12 °C (flow rate: 0.70 mL/min). Chromatograms were analyzed using Astra 6.0 software.

**Surface plasmon resonance (SPR).** All experiments were performed on a Biacore T100 instrument with a Series S CM5 chip (GE Healthcare Life Sciences). The procedure used here was modified from a published procedure by Safina *et al.* The running buffer was 10 mM HEPES buffer (pH 7.4) with 0.005% Tween P20, 1 mM CaCl$_2$, 1 mM MgCl$_2$, and 1 mM MnCl$_2$. 5 μL/min flow rate was used throughout the experiments. First, a reference channel (flow cell 1) was prepared by activating the surface with a 0.4 M EDC and 0.1 M NHS (1:1 v/v) mixture during 30 minutes, then 1 M ethanolamine HCl (pH 8.5) during 40 minutes. Then, the sample channel (flow cell 2) was activated using under the EDC/NHS conditions, followed by injection of 0.1 mg/mL...
ConA for 40 minutes and then 1 M ethanolamine HCl for 30 minutes for blocking. Analyte samples of 0.022 μM to 130 μM were injected in tandem over both cells for 6 minutes. Surfaces were regenerated by injecting 10 mM HCl for 2 minutes followed by injecting 10 mM glycine HCl (pH 2.5) for 2 minutes. Binding curves at various analyte concentrations were fitted to the Langmuir 1:1 binding model for an estimation of the binding constants. For the purpose of figure presentation, the sensorgrams were processed using the smoothing function in the OriginPro data analysis software.

**X-ray data collection and processing parameters.** For 2, a single crystal was mounted on a nylon loop using perfluoropolyether oil and cooled rapidly to 100 K with a stream of cold dinitrogen. Diffraction data were measured using a Bruker APEX-II CCD diffractometer using Mo-Kα radiation. The cell refinement and data reduction were carried out using Bruker SAINT and the structure was solved with SHELXS-97. All subsequent crystallographic calculations were performed using SHELXL-2013. For 3, single-crystal diffraction data were collected at 100(2) K on a Bruker Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). After correcting for absorption and polarization effects, structure solution and refinement were carried out using the SHELXT2, XL3 and Olex24 software suites. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms were placed in suitable riding positions.
| compound | 3 |
|---|---|
| empirical formula | C\textsubscript{78}H\textsubscript{36}B\textsubscript{6}F\textsubscript{30}O\textsubscript{6} |
| fw | 1703.95 |
| temp / K | 100 |
| wavelength / Å | 0.71073 Å |
| space group | \( P \mathbf{-1} \) |
| \( a / \text{Å} \) | 19.211(3) |
| \( b / \text{Å} \) | 19.674(3) |
| \( c / \text{Å} \) | 22.866(4) |
| \( a / \text{deg} \) | 97.606(5) |
| \( \beta / \text{deg} \) | 114.089(5) |
| \( \gamma / \text{deg} \) | 109.756(5) |
| \( V / \text{Å}^3 \) | 7047.9(18) |
| \( Z \) | 2 |
| \( d \text{ (calcd) / Mg}\cdot\text{m}^{-3} \) | 1.606 |
| \( \text{abs coeff / mm}^{-1} \) | 0.153 |
| \( R \text{ indices:} \) | \( R_I = 0.1771 \) |
| | \( R_w = 0.2030 \) |

**Microwave synthesis.** Microwave reactions were performed using a CEM Discover SP microwave synthesis reactor. Except where noted otherwise, all reactions were performed in glass 10 mL microwave reactor vials purchased from CEM with silicone/PTFE caps. Flea micro PTFE-coated stir bars (10 mm x 3 mm) were used in the vials with magnetic stirring set to high and 15 seconds of premixing prior to the temperature ramping. All microwave reactions were carried out at 140 °C with the pressure release limit set to 250 psi (no reactions exceeded this limit to trigger venting) and the maximum wattage set to 250 W (the power applied was dynamically controlled by the microwave instrument and did not exceed this limit for any reactions). Column chromatography was performed using 2.0 - 2.25 cm inner diameter glass fritted chromatography columns with 20-30 cm of slurry-packed silica gel to ensure full separation of reagents and products. Unfiltered pressurized air was used to assist column chromatography.
Synthesis of 1

The \( [\text{N}^n\text{Bu}_4]_2 \) salt of \( [\text{B}_{12}(\text{OH})_{12}]^{2-} \) was prepared according to the procedures detailed in Wixtrom et al. 2016.\(^5\) From this point, \( \text{N}^n\text{Bu}_4 \) will be referred to as TBA. Note: \( 1 \) is air-stable, but hygroscopic. Store under inert atmosphere or in a sealed desiccator to prevent excess absorption of water over extended periods of time in storage.

Synthesis of 2

Previously reported protocol\(^6\) used to synthesize compound 2 – procedure is duplicated here. Compound 1 (300 mg, 0.366 mmol) was transferred out of a nitrogen filled glovebox, opened to the air, and dissolved in 4 mL acetonitrile in a 30 mL glass microwave vial. \( N,N\)-diisopropylethylamine (1.21 mL, 6.96 mmol) and 2,3,4,5,6-pentafluorobenzyl bromide (6.86 mL 45.4 mmol) were added along with a magnetic stir bar, the vial was sealed with a Teflon/silicone cap, and the reaction mixture was heated under microwave conditions at 140°C with high stirring for 15 minutes. The volatiles were removed via rotary evaporation, and the excess reagent was eluted through a silica column with 65/35 hexanes/ethyl acetate, and the pink/purple product mixture was eluted with acetone. The acetone was removed via rotary evaporation and the residue was dissolved in ~5 mL 90/5/5 ethanol/acetonitrile/H\(_2\)O. \( \text{FeCl}_3\cdot6\text{H}_2\text{O} \) (1.88 g, 6.96 mmol) was added and the mixture was left to stir for 24 hours. The mixture was concentrated in vacuo. The
residue (while still in the round bottom flask) was rinsed three times with water. The residue was then taken up in toluene and extracted three times with water. The organic fractions were combined and dried under vacuum. The resulting solid was charged with hexane and isolated by filtration to afford an orange/yellow solid (574 mg, 63%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.23 (s, 24H). $^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ 40.9. $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 60.1. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -145.1 (d, 24F, -ortho), -152.2 (t, 12F, -para), -161.3 – -161.5 (m, 24F, -meta). HRMS (Q-Exactive Plus): $m/z$ calculated for C$_{84}$H$_{84}$B$_{12}$O$_{12}$ (M$^-$), 2494.1499 Da; found, 2494.1631 Da. Crystallized from CDCl$_3$ at room temperature for 1 week to obtain a single crystal for X-ray diffraction analysis.

**Synthesis of 4-pentafluorophenyl(hydroxymethyl) benzene**

![Chemical structure](image)

A solution of 4-pentafluorophenyl benzaldehyde (0.900 g, 3.30 mmol) and sodium borohydride (0.150 g, 3.96 mmol) in 14 mL tetrahydrofuran and 7 mL ethanol was prepared and placed under a positive nitrogen flow. The mixture was stirred at room temperature for 24 hours. The resulting dark solution was diluted with water (30 mL) and extracted with methylene chloride (30 mL). The organic layer was washed three times with H$_2$O, dried over MgSO$_4$, and filtered through Celite. The solvent was then dried *in vacuo*. The residue was purified by flash chromatography (eluent: DCM; $R_f = 0.4$) through a silica column, using UV light for TLC visualization. The resulting solution was dried under vacuum, providing 4-pentafluorophenyl(hydroxymethyl) benzene as a white solid (0.705 g, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (d, 2H, Ar), 7.42 (d, 2H, Ar), 4.76 (d, 2H, CH$_2$OH), 2.05 (t, 1H, CH$_2$OH). $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 144.3, 142.3, 140.6,
138.1, 130.5, 127.2, 126.3, 115.8, 64.9. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -143.3 (q, 2F, -ortho), -155.5 (t, 1F, -para), -162.2 (m, 2F, -meta).

**Synthesis of 4-pentafluorophenyl(bromomethyl) benzene**

![Diagram of 4-pentafluorophenyl(bromomethyl) benzene]

A flask containing 4-pentafluorophenyl(hydroxymethyl) benzene (1.00 g, 3.65 mmol) was purged with nitrogen and 30 mL of dry methylene chloride was charged into the flask. The solution was placed in ice bath and PBr$_3$ (346 $\mu$L, 3.65 mmol) was added via syringe. The reaction mixture was stirred overnight, during which time the mixture turned yellow. The resulting mixture was then diluted with 100 mL distilled H$_2$O. The organic layer was separated and washed 3 times with saturated NaCl solution. Organic layer was collected and dried over MgSO$_4$, then filtered through Celite. Solvent was evaporated and the residue was purified by flash chromatography (hexane/CH$_2$Cl$_2$, 2:1; $R_f = 0.75$) through a silica column, using UV light for TLC visualization. The resulting solution was dried under vacuum, providing 4-pentafluorophenyl(bromomethyl) benzene as a white solid (0.773 g, 63%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.53 (d, 2H, Ar), 7.42 (d, 2H, Ar), 4.54 (s, 2H, CH$_2$Br). $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 144.3, 140.7, 139.1, 138.0, 130.7, 129.5, 126.6, 115.4, 32.6. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -143.1 (q, 2F, -ortho), -155.1 (t, 1F, -para), -162.0 (m, 2F, -meta).

**Synthesis of 3**

![Diagram of 3]
Compound 1 (75.0 mg, 0.092 mmol) was added to a 10 mL glass microwave vial and transferred out of a nitrogen-filled glovebox, opened to the air, and dissolved in 1.5 mL acetonitrile. *N*-*N*-diisopropylethylamine (0.3 mL, 1.73 mmol) and 4-pentafluorophenyl(bromomethyl) benzene (0.8334 g, 2.47 mmol) were added along with a flea micro stir bar, the vial was sealed with a PTFE/silicone cap, and the mixture was heated at 140 °C with stirring in the microwave for 30 minutes. The volatiles were removed via rotary evaporation, and the remaining reagent was eluted first through a slurry-packed silica gel column with 80/20 hexanes/CH₂Cl₂, and the pink/purple product mixture was eluted with acetone followed by CH₂Cl₂. *Note: The eluted fraction containing the reagent ligand can be purified by eluting through a silica column with 90/10 hexanes/CH₂Cl₂, and after drying thoroughly it can be used for subsequent synthesis of 3. Recycling the ligand in this manner can minimize unnecessary repetition of ligand synthesis.* The volatiles were removed via rotary evaporation, and the remaining charged 2-/1- product mixture was dissolved in 5 mL 90/10 EtOH/MeCN. FeCl₃·6H₂O (0.3 g, 1.11 mmol) was added and the mixture was left to stir for 24 hours. Following oxidation, the solvent mixture was removed via rotary evaporation, and a red-orange band containing the neutral product was separated from the FeCl₃·6H₂O through a slurry-packed silica gel column with CH₂Cl₂. The CH₂Cl₂ was removed via rotary evaporation and the final neutral product 2 was dried under high vacuum to obtain an isolated yield of 266.5 mg (85%).

Compound 2 is a dark red-orange solid. "H NMR (500 MHz, CD₂Cl₂): δ 7.21 - 7.33 (m, 48H, C₆H₄), 5.50 (s, 24H, OCH₂). "B {"H} NMR (128 MHz, CD₂Cl₂): δ 42.4. "F NMR (376 MHz, CD₂Cl₂): δ -144.2 (q, 24F, -ortho), -156.5 (t, 12F, -para), -163.4 – -163.5 (m, 24F, -meta). HRMS (Q-Exactive Plus): m/z calculated for C₁₆₅H₇₂B₁₂F₆₀O₁₂ (M⁺), 3407.5289 Da; found, 3407.5278 Da. X-ray quality crystals of 3 were grown from a cooling solution of boiling 1:1 EtOH:MeOH.
Supplementary Table 1. Initial Studies and Reaction Optimization

| Entry | Base     | Yield<sup>a</sup> (%) |
|-------|----------|-----------------------|
| 1     | NEt<sub>3</sub> | 3                     |
| 2     | Tris     | 7                     |
| 3     | K<sub>3</sub>PO<sub>4</sub> | 72                   |
| 4     | K<sub>2</sub>CO<sub>3</sub> | 87                   |

<sup>a</sup>Yield determined by <sup>19</sup>F NMR. Tris, tris(hydroxymethyl)aminomethane.

Synthesis of 2a

2 (5.0 mg, 0.0020 mmol) and K<sub>2</sub>CO<sub>3</sub> (8.4 mg, 0.061 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N<sub>2</sub> three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by 1-hexanethiol (3.76 μL, 0.027 mmol). The vial was sealed again and set to stir at 400 rpm for 22 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for <i>in situ</i> <sup>19</sup>F NMR spectroscopy to ensure nearly quantitative conversion and <i>in situ</i> <sup>11</sup>B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur
pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 2a was loaded onto the column with 80/20 hexanes/ethyl acetate (sonication was used to aid dissolution), and the remaining reagent was eluted with 80/20 hexanes/ethyl acetate. A very slightly yellow band containing 2a was eluted with MeCN, and the fractions containing 2a (as assessed by TLC) were combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 5.4 mg (70%). $^1$H NMR (400 MHz, CD$_3$CN): δ 5.42 (br s, 24H, OCH$_2$), 3.12 (q, 12H, [(CH$_3$CH$_2$)$_3$NH]$^+$), 2.89 – 2.82 (m, 24H, SCH$_2$), 1.49 - 1.39 (m, 24H, SCH$_2$CH$_2$), 1.36 – 1.26 (br m, 24H, S(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 1.24 (t, 18H, [(CH$_3$CH$_2$)$_3$NH]$^+$), 1.21 – 1.10 (br m, 48H, S(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 0.83 – 0.74 (m, 36H, S(CH$_2$)$_5$CH$_3$). $^{11}$B$^1$H NMR (128 MHz, CD$_3$CN): δ -15.8. $^{19}$F NMR (376 MHz, CD$_3$CN): δ -137.4 (br m, 24F, -meta$^7$), -145.1 (br m, 24F, -ortho$^7$). MS (LCT Premier): m/z calculated for C$_{156}$H$_{180}$B$_{12}$F$_{48}$O$_{12}$S$_{12}$ (M$^+$), 1836.52 Da; found, 1836.29 Da.

**Synthesis of 2b**

2 (5.0 mg, 0.0020 mmol) and K$_3$PO$_4$ (9 mg, 0.042 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 µL anhydrous DMF was added, followed by thiophenol (2.66 µL, 0.026 mmol). The vial was sealed again and set to stir at 400 rpm for 25 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR
tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 2b was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing 2b was eluted with MeCN, and the fractions containing 2b (as assessed by TLC) were combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 6.8 mg (90%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 7.22 – 7.14 (br m, 60H, S-Ar), 5.49 (br s, 24H, OCH$_2$), 3.11 (q, 12H, [(CH$_3$CH$_2$)$_3$NH$^+$]), 1.23 (t, 18H, [(CH$_3$CH$_2$)$_3$NH$^+$]). $^{11}$B{$^1$H} NMR (128 MHz, CD$_3$CN): $\delta$ -15.7. $^{19}$F NMR (376 MHz, CD$_3$CN): $\delta$ -136.4 (m, 24F, -meta), -144.1 (m, 24F, -ortho). HRMS (Q-Exactive Plus): $m/z$ calculated for C$_{156}$H$_{84}$B$_{12}$F$_{48}$O$_{12}$S$_{12}$ (M$^2^+$), 1788.1481 Da; found, 1788.1514 Da.

**Synthesis of 2c**

![Diagram of 2c](image)

2 (5.0 mg, 0.0020 mmol) and K$_3$PO$_4$ (8.1 mg, 0.038 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 µL anhydrous DMF was added, followed by benzyl mercaptan (3.53 µL, 0.030 mmol). The vial was sealed again and set to stir at
400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 2c was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing 2c was eluted with MeCN, and the fractions containing 2c (as assessed by TLC) were combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 7.4 mg (93.5%). $^1$H NMR (400 MHz, CD$_3$CN): δ 7.20 – 7.04 (br m, 60H, SCH$_2$-Ar), 5.39 (br s, 24H, OCH$_2$), 4.05 (m, 24H, SCH$_2$), 3.11 (q, 12H, [(CH$_3$CH$_2$)$_3$NH]$^+$), 1.23 (t, 18H, [(CH$_3$CH$_2$)$_3$NH]$^+$). $^{11}$B{$^1$H} NMR (128 MHz, CD$_3$CN): δ -15.8. $^{19}$F NMR (376 MHz, CD$_3$CN): δ -136.8 (m, 24F, -meta), -144.8 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{168}$H$_{108}$B$_{12}$F$_{48}$O$_{12}$S$_{12}$ (M$^+$), 1872.2420 Da; found, 1872.2469 Da.

**Synthesis of 2d**

![Image of 2d structure]

2 (5.0 mg, 0.0020 mmol) and K$_3$PO$_4$ (10.4 mg, 0.049 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred
into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added, followed by 2-mercaptoethanol (2.26 μL, 0.032 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 2d was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 2.6 mg (40 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 5.50 (br s, 24H, OCH$_2$), 3.64 (t, 24H, CH$_2$CH$_2$OH), 3.00 (t, SCH$_2$CH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.7. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -137.6 – -137.7 (m, 24F, -meta), -145.1 – -145.2 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{108}$H$_{84}$B$_{12}$F$_{48}$O$_{24}$S$_{12}$ (M$^+$), 1596.1176 Da; found, 1596.1233 Da.

**Synthesis of 2e**

![Image of 2e](image)

2 (5.0 mg, 0.0020 mmol) and K$_3$PO$_4$ (10.2 mg, 0.048 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added,
followed by thioglycerol (3.12 μL, 0.036 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ ¹⁹F NMR spectroscopy to ensure nearly quantitative conversion and in situ ¹¹B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 2e was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via ¹H, ¹¹B, and ¹⁹F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 2.2 mg (30%). ¹H NMR (400 MHz, CD₃OD): δ 5.50 (br s, 24H, OCH₂), 3.69 – 3.64 (m, 12H, SCH₂CH(OH)), 3.60 – 3.53 (m, 24H, CH(OH)CH₂OH), 3.07 – 2.93 (m, 24H, SCH₂CH(OH)). ¹¹B NMR (128 MHz, CD₃OD): δ -15.6. ¹⁹F NMR (376 MHz, CD₃OD): δ -137.5 – -137.6 (m, 24F, -meta), -145.1 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C₁₂₀H₁₀₈B₁₂F₄₈O₃₆S₁₂ (M⁺), 1776.1810 Da; found, 1776.1894 Da.

**Synthesis of 2f**

2 (5.0 mg, 0.0020 mmol) and K₂CO₃ (2.6 mg, 0.019 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N₂ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 μL anhydrous DMF was added,
followed by cysteamine (3.7 mg, 0.048 mmol). The vial was sealed again and set to stir at 400 rpm for 23 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for \textit{in situ} $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and \textit{in situ} $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in 40/60 MeOH/MeCN (23 cm packed height), and the crude product mixture containing 2f was loaded onto the column with 40/60 MeOH/MeCN. 15 1-2 mL fractions were collected, dried \textit{via} rotary evaporation, and subjected to characterization \textit{via} $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried \textit{via} rotary evaporation to obtain an isolated yield of 3.2 mg (49 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 5.51 (br s, 24H, OCH$_2$), 2.94 (t, 24H, SCH$_2$CH$_2$), 2.72 (t, CH$_2$CH$_2$NH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.4. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -137.6 (m, 24F, -meta), -144.4 – -144.6 (m, 24F, -ortho). MS (LCT Premier): m/z calculated for C$_{108}$H$_{96}$B$_{12}$F$_{48}$N$_{12}$O$_{12}$S$_{12}$ (M$^+$), 1590.21 Da; found, 1590.07 Da.

\textbf{Synthesis of 2i}

![Image of compound 2i]

2 (8 mg, 0.0032 mmol) and K$_3$PO$_4$ (16.6 mg, 0.078 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 240 µL anhydrous DMF was added, followed by mPEGthiol$_{356}$ (20.63 µL, 0.064 mmol). The vial was sealed again and set to stir at 400 rpm for
28 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for \textit{in situ} $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and \textit{in situ} $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 2i was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried \textit{via} rotary evaporation, and subjected to characterization \textit{via} $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried \textit{via} rotary evaporation to obtain an isolated yield of 16.9 mg (81 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 5.51 (br s, 24H, OCH$_2$), 3.63 – 3.50 (m, 312H, SCH$_2$CH$_2$O(CH$_2$CH$_2$O)$_6$), 3.35 – 3.33 (m, 36H, (CH$_2$CH$_2$O)$_6$CH$_3$), 3.08 (t, 24H, SCH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.7. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -137.2 – -137.3 (m, 24F, -meta), -144.8 (m, 24F, -ortho). HRMS (Q-Exactive Plus): \textit{m/z} calculated for C$_{264}$H$_{396}$B$_{12}$F$_{48}$O$_{96}$S$_{12}$ (M$^2$), 3265.1552 Da; found, 3265.1444 Da.

\textbf{Synthesis of j}

\textbf{1. Synthesis of j-Br}

\begin{center}
\includegraphics[width=0.5\textwidth]{j-br.png}
\end{center}

In a round bottom flask, mPEG$_{750}$ (7.50 g, 10.00 mmol) and CBr$_4$ (3.98 g, 12.00 mmol) were dissolved in 40 mL of acetonitrile. To the stirring solution, PPh$_3$ (3.15 g, 6.00 mmol) was added in small portions over 30 minutes. The mixture was then left stirring at room temperature for 4 hours. After 4 hours, the solvent was then removed \textit{in vacuo} and the resulting yellow-orange oil was dissolved in 20 mL of H$_2$O and left at 4 °C overnight, producing a white precipitate. The mixture was filtered through Celite* on a glass frit and the filtrate was washed twice with 5 mL of
toluene. The aqueous layer was dried *in vacuo* to yield the desired product as an orange oil (7.08 g, 87%). 1H NMR (400 MHz, CDCl3): δ 3.55 – 3.51 (m, 62H, CH₂O(CH₂CH₂O)₁₅), 3.43 (m, 2H, BrCH₂), 3.26 (s, 3H, (CH₂CH₂O)₁₅CH₃).

*Celite was pretreated on the frit by washing with 30 mL of H₂O before the mixture was filtered.

2. Synthesis of j-SA

![Chemical Structure](attachment:image.png)

To a solution of j-Br (1.07 g, 1.32 mmol) in 35 mL of ethanol, potassium thioacetate (0.20 g, 1.75 mmol) was added in one portion. The mixture was refluxed at 120 °C for 5 hours. The resulting suspension was filtered through Celite and the filtrate was dried under vacuum, affording a brown oil. The oil was dissolved in 40 mL of chloroform and the organic phase was washed twice with H₂O. The organic layer was dried over Na₂SO₄ and filtered through Celite. The solvent was removed *in vacuo*, providing j-SA (0.64 g, 74%). 1H NMR (400 MHz, CDCl₃): δ 3.64 – 3.61 (m, 62H, CH₂O(CH₂CH₂O)₁₅), 3.36 (s, 3H, (CH₂CH₂O)₁₅CH₃), 3.07 (t, 2H, SCH₂), 2.32 (s, 3H, SCOCH₃).

3. Synthesis of j

![Chemical Structure](attachment:image.png)

j-SA (405 mg, 0.5 mmol) was charged with 5 mL of 1M HCl and was refluxed at 110 °C for 2 hours under a blanket of Ar. The solvent was removed *in vacuo*. The residue was dissolved in 10 mL of DCM and the organic phase was washed twice with water. The organic layer was separated and dried over Na₂SO₄ and filtered through Celite. The solution was dried under vacuum to yield the desired product as a brown oil (319 mg, 83%). Product was stored under inert atmosphere. 1H
NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 3.58 – 3.59 (m, 62H, CH$_2$O(CH$_2$CH$_2$O)$_{15}$), 3.32 (s, 3H, (CH$_2$CH$_2$O)$_{15}$CH$_3$), 2.67 (dt, 2H, SHCH$_2$), 1.61 (t, 1H, SHCH$_2$).

**Synthesis of 2j**

2 (5.0 mg, 0.0020 mmol) and K$_3$PO$_4$ (19.2 mg, 0.090 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 $\mu$L anhydrous DMF was added, followed by mPEGthiol$_{766}$ (48.1 $\mu$L, 0.069 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing 2j was loaded onto the column with water. 15 1-2 mL fractions were collected, dried *via* lyophilization, and subjected to characterization *via* $^{1}$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried *via* lyophilization to obtain an isolated yield of 4.4 mg (19%). $^{1}$H NMR (400 MHz, CD$_3$OD): $\delta$ 5.50 (br s, 24H, OCH$_2$), 3.63 – 3.53 (m, 744H, SICH$_2$O(CH$_2$CH$_2$O)$_{15}$), 3.35 (m, 36H, (CH$_2$CH$_2$O)$_{15}$CH$_3$), 3.08 (t, 24H, SICH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): $\delta$ -16.0. $^{19}$F NMR (376 MHz, CD$_3$OD): $\delta$ -137.2 (m, 24F, *-meta*), -144.8 (m, 24F, *-ortho*).
Synthesis of 2k

2 (5.0 mg, 0.0020 mmol) and K₃PO₄ (13.4 mg, 0.063 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N₂ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 µL anhydrous DMF was added, followed by mPEGthiol₂₀₀₀ (101.0 mg, 0.051 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ ¹⁹F NMR spectroscopy to ensure nearly quantitative conversion and in situ ¹¹B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing 2k was loaded onto the column with water. 15 1-2 mL fractions were collected, dried via lyophilization, and subjected to characterization via ¹H, ¹¹B, and ¹⁹F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via lyophilization to obtain an isolated yield of 21.5 mg (41%). ¹H NMR (400 MHz, CD₃OD): δ 5.50 (br s, 24H, OCH₂), 3.82 – 3.45 (m, 2100H, SCH₂CH₂(CONH)CH₂CH₂O(CH₂CH₂O)₄₂), 3.36 (s, 36H, (CH₂CH₂O)₄₂CH₃), 3.09 (t, 24H, SCH₂CH₂). ¹¹B NMR (128 MHz, CD₃OD): δ -16.0. ¹⁹F NMR (376 MHz, CD₃OD): δ -137.0 – -137.1 (m, 24F, -meta), -144.8 (m, 24F, -ortho). GPC trace of 2k measured in water with 0.02% NaN₃ at 12 °C gives a Ð (polydispersity index) of 1.003 (see Fig. 3c in main text).
Synthesis of 2l

2 (5.0 mg, 0.0020 mmol) and K₃PO₄ (13.0 mg, 0.061 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N₂ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 150 µL anhydrous DMF was added, followed by 1-thio-β-D-glucose tetraacetate (25.0 mg, 0.069 mmol). The vial was sealed again and set to stir at 400 rpm for 24 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ ¹⁹F NMR spectroscopy to ensure nearly quantitative conversion and in situ ¹¹B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. The resulting residue was treated with NaOMe (6.0 mg, 0.11 mmol) in 1 mL MeOH for 2 hours. The volatiles were removed via rotary evaporation. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing 2l was loaded onto the column with water. 15 1-2 mL fractions were collected, dried via lyophilization, and subjected to characterization via ¹H, ¹¹B, and ¹⁹F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via lyophilization to obtain an isolated yield of 1.6 mg (17 %). ¹H NMR (400 MHz, D₂O): δ 5.64 – 5.45 (br s, 24H, OCH₂), 4.03 – 3.20 (m, 84H, SCHCH₂OH(CH₂OH)₃CHO). ¹¹B NMR (128 MHz, D₂O): δ -16.3. ¹⁹F NMR (376 MHz, D₂O): δ -134.3 – -135.6 (m, 24F, -meta), -143.5 (m, 24F, -
ortho). HRMS (Q-Exactive Plus): m/z calculated for C₁₅₆H₁₅₆B₁₂F₄₈O₇₂S₁₂ (M⁻), 2304.2772 Da; found, 2304.2769 Da.

**Synthesis of 3a**

3 (10.0 mg, 0.0029 mmol) and K₂CO₃ (22.0 mg, 0.159 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N₂ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by 1-hexanethiol (5.42 µL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 7 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ ¹⁹F NMR spectroscopy to ensure nearly quantitative conversion and in situ ¹¹B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 3a was loaded onto the column with 80/20 hexanes/ethyl acetate (sonication was used to aid dissolution), and the remaining reagent was eluted with 80/20 hexanes/ethyl acetate. A very slightly yellow band containing 3a was eluted with MeCN, and the fractions containing 3a (as assessed by TLC) were combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 12.2 mg (87%). ¹H NMR (400 MHz, CD₃CN): δ 7.64 – 7.50 (br m, 24H, OCH₂-Ar), 7.25 – 7.15 (br m, 24H, OCH₂-Ar), 5.60 (br s, 24H, OCH₃), 3.06 (q, 12H,
[(CH$_3$CH$_2$)$_3$NH]$^+$, 2.93 (t, 24H, S(CH$_2$)$_2$), 1.61 - 1.49 (m, 24H, S(CH$_2$)$_2$CH$_3$), 1.44 – 1.34 (br m, 24H, S(CH$_2$)$_2$(CH$_2$)$_2$CH$_3$), 1.30 – 1.21 (br m, 48H, S(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 1.18 (t, 18H, [(CH$_2$CH$_2$)$_3$NH]$^+$), 0.89 – 0.80 (m, 36H, S(CH$_2$)$_5$CH$_3$). $^{11}$B [$^1$H] NMR (128 MHz, CD$_3$CN): δ -15.1. $^{19}$F NMR (376 MHz, CD$_3$CN): δ -136.7 (q, 24F, -meta), -145.2 (q, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{228}$H$_{228}$B$_{12}$F$_{48}$O$_{12}$S$_{12}$ (M$^2$-) 2292.7115 Da; found, 2292.7157 Da.

**Synthesis of 3b**

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (18.9 mg, 0.089 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by thiophenol (3.89 µL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 7 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 3b was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing 3b was eluted with MeCN, and the fractions containing 3b (as assessed by TLC) were
combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 11.7 mg (85%). \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 7.65 – 7.48 (br m, 24H, OCH\(_2\)-Ar), 7.34 – 7.20 (br m, 60H and 24H, S-Ar and OCH\(_2\)-Ar), 5.61 (br s, 24H, OCH\(_2\)), 3.09 (q, 12H, [(CH\(_3\)CH\(_2\))\(_3\)NH]\(^+\)), 1.21 (t, 18H, [(CH\(_3\)CH\(_2\))\(_3\)NH]\(^+\)). \(^{11}\)B\(^{\text{\(\text{\textit{\textit{H}}}\)}}\) NMR (128 MHz, CD\(_3\)CN): \(\delta\) -15.1. \(^{19}\)F NMR (376 MHz, CD\(_3\)CN): \(\delta\) -135.9 (m, 24F, -meta), -145.2 (m, 24F, -ortho). HRMS (Q-Exactive Plus): \(m/z\) calculated for C\(_{228}\)H\(_{132}\)B\(_{12}\)F\(_{48}\)O\(_{12}\)S\(_{12}\) (M\(^2+\)), 2244.3359 Da; found, 2244.3381 Da.

**Synthesis of 3c**

![Diagram of 3c]

3 (10.0 mg, 0.0029 mmol) and K\(_3\)PO\(_4\) (22.5 mg, 0.106 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N\(_2\) three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 \(\mu\)L anhydrous DMF was added, followed by benzyl mercaptan (4.48 \(\mu\)L, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ \(^{19}\)F NMR spectroscopy to ensure nearly quantitative conversion and in situ \(^{11}\)B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 5 ¾” glass Pasteur pipet column was prepared using glass wool and 4” of silica gel, and the pipet was flushed with triethylamine (2X column volumes). The crude product mixture containing 3c was loaded onto the column with 35/65 ethyl acetate/hexanes (sonication was used to aid dissolution), and the
remaining reagent was eluted with 35/65 ethyl acetate/hexanes. A very slightly yellow band containing 3c was eluted with MeCN, and the fractions containing 3c (as assessed by TLC) were combined and volatiles were removed via rotary evaporation followed by lyophilization overnight to obtain an isolated yield of 11.6 mg (81%). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 7.59 – 7.52 (br d, 24H, OCH$_2$-Ar), 7.26 – 7.15 (br m, 60H and 24H, SCh$_2$-Ar and OCH$_2$-Ar), 5.60 (br s, 24H, OCH$_2$), 4.11 (br s, 24H, SCh$_2$), 3.06 (q, 12H, [(CH$_3$CH$_2$)$_3$NH]$^+$), 1.18 (t, 18H, [(CH$_3$CH$_2$)$_3$NH]$^+$). $^{11}$B {$^1$H} NMR (128 MHz, CD$_3$CN): $\delta$ -15.1. $^{19}$F NMR (376 MHz, CD$_3$CN): $\delta$ -135.9 (q, 24F, -meta), -145.1 (q, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{240}$H$_{150}$B$_{12}$F$_{48}$O$_{12}$S$_{12}$ (M$^+$), 2328.9298 Da; found, 2328.9363 Da.

**Synthesis of 3d**

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (12.3 mg, 0.058 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 $\mu$L anhydrous DMF was added, followed by 2-mercaptoethanol (2.69 $\mu$L, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed
height), and the crude product mixture containing 3d was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 10.0 mg (81 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 7.61 – 7.45 (br m, 24H, OCH$_2$-Ar), 7.24 – 7.13 (br m, 24H, OCH$_2$-Ar), 5.65 (br m, 24H, OCH$_2$), 3.73 (t, 24H, CH$_2$CH$_2$OH), 3.10 (t, SCH$_2$CH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.1. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -136.8 – -136.9 (m, 24F, -meta), -145.4 – -145.5 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{180}$H$_{132}$B$_{12}$F$_{48}$O$_{24}$S$_{12}$ (M$^2$), 2052.3054 Da; found, 2052.3080 Da.

**Synthesis of 3e**

![](image)

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (13.1 mg, 0.062 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by thioglycerol (3.30 µL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the
crude product mixture containing 3e was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 7.9 mg (59%). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 7.59 – 7.45 (br m, 24H, OCH$_2$-Ar), 7.23 – 7.16 (br m, 24H, OCH$_2$-Ar), 5.64 – 5.60 (br m, 24H, OCH$_2$), 3.78 – 3.72 (m, 12H, SCH$_2$CH(OH)), 3.65 – 3.57 (m, 24H, CH(OH)CH$_2$OH), 3.17 – 3.02 (m, 24H, SCH$_2$CH(OH)). $^{11}$B NMR (128 MHz, CD$_3$OD): $\delta$ -15.1. $^{19}$F NMR (376 MHz, CD$_3$OD): $\delta$ -136.6 – -136.7 (m, 24F, -meta), -145.5 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{192}$H$_{156}$B$_{12}$F$_{48}$O$_{36}$S$_{12}$ (M$^+$), 2232.3688 Da; found, 2232.3752 Da.

**Synthesis of 3f**

![image](image.png)

3 (10.0 mg, 0.0029 mmol) and K$_2$CO$_3$ (8.1 mg, 0.059 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 $\mu$L anhydrous DMF was added, followed by cysteamine (4.9 mg, 0.064 mmol). The vial was sealed again and set to stir at 400 rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in 40/60 MeOH/MeCN (23 cm packed height),
and the crude product mixture containing 3f was loaded onto the column with 40/60 MeOH/MeCN. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via 1H, 11B, and 19F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 4.0 mg (33%). 1H NMR (400 MHz, 33/67 CD3OD/CD3CN): δ 7.55 – 7.52 (br m, 24H, OCH2-Ar), 7.21 – 7.18 (br m, 24H, OCH2-Ar), 5.60 – 5.54 (br m, 24H, OCH2), 2.95 (t, 24H, SCH2CH2), 2.70 (t, CH2CH2NH2). 11B NMR (128 MHz, 33/67 CD3OD/CD3CN): δ -15.2. 19F NMR (376 MHz, 33/67 CD3OD/CD3CN): δ -136.0 – -136.5 (m, 24F, -meta), -145.1 – -145.6 (m, 24F, -ortho). MS (LCT Premier): m/z calculated for C180H144B12F48N12O12S12 (M2−), 2046.40 Da; found, 2046.31 Da.

Synthesis of 3g

3 (10.0 mg, 0.0029 mmol) and K3PO4 (18.7 mg, 0.088 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N2 three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by N-(tert-Butoxycarbonyl)-L-cysteine methyl ester (8.16 µL, 0.040 mmol). The vial was sealed again and set to stir at 400 rpm for 3 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ 19F NMR spectroscopy to ensure nearly quantitative conversion and in situ 11B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for
solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 3g was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 8.8 mg (49 %). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 7.52 (d, 24H, OCH$_2$-Ar), 7.19 (d, 24H, OCH$_2$-Ar), 5.63 (br s, 24H, OCH$_2$), 4.37 – 4.34 (br m, 12H, SCH$_2$CH), 3.69 (m, 36H, OCH$_3$), 3.49 – 3.44 (br m, 24H, SCH$_2$), 1.35 – 1.33 (m, 24H, C(CH$_3$)$_3$). $^{11}$B NMR (128 MHz, CD$_3$OD): $\delta$ -15.1. $^{19}$F NMR (376 MHz, CD$_3$OD): $\delta$ -135.9 – -136.0 (m, 24F, -meta), -144.8 – -145.1 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{264}$H$_{264}$B$_{12}$F$_{48}$N$_{12}$O$_{60}$S$_{12}$ (M$^2$-), 2994.7487 Da; found, 2994.7404 Da.

Synthesis of 3h

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (56.1 mg, 0.264 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 $\mu$L anhydrous DMF was added, followed by unprotected C-A-G·TFA (synthesized using conventional Fmoc solid-phase peptide synthesis protocol$^8$) (17.8 mg, 0.049 mmol) and isopropoxyltrimethylsilane (18.8 $\mu$L, 0.106 mmol). The vial was sealed again and set to stir at 400 rpm for 6 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR
spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in H$_2$O/ACN (23 cm packed height), and the crude product mixture containing 3h was loaded onto the column with H$_2$O/ACN. 15 1-2 mL fractions were collected, dried via lyophilization, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via lyophilization to obtain an isolated yield of 5.3 mg (29%). $^1$H NMR (400 MHz, D$_2$O/CD$_3$CN): $\delta$ 7.44 (br m, 24H, OCH$_2$-Ar), 7.09 – 7.08 (br m, 24H, OCH$_2$-Ar), 5.50 (br s, 24H, O-CH$_2$), 3.77 – 3.68 (br m, 24H, (CONH)CH$_2$(CONH$_2$)), 3.48 – 3.45 (br t, 12H, SCH$_2$CH), 3.15 – 3.10 (br m, 24H, SCH$_2$), 1.26 – 1.24 (d, 36H, CCH$_3$). $^{11}$B NMR (128 MHz, D$_2$O/CD$_3$CN): $\delta$ -15.8. $^{19}$F NMR (376 MHz, D$_2$O/CD$_3$CN): $\delta$ -135.4 – -135.5 (m, 24F, -meta), -144.7 – -144.8 (m, 24F, -ortho). MS (LCT Premier): m/z calculated for C$_{252}$H$_{252}$B$_{12}$F$_{48}$N$_{48}$O$_{48}$S$_{12}$ (M$^{2+}$), 3072.79 Da; found, 3072.60 Da.

**Synthesis of 3i**

![Image](image-url)

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (8.5 mg, 0.040 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by mPEGthiol$_{356}$ (12.27 µL, 0.038 mmol). The vial was sealed again and set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred
into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 3i was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 17.1 mg (78 \%). $^1$H NMR (400 MHz, CD$_3$OD): δ 7.64 – 7.46 (br m, 24H, OCH$_2$-Ar), 7.26 – 7.18 (br m, 24H, OCH$_2$-Ar), 5.65 – 5.61 (br m, 24H, OCH$_2$), 3.70 (t, 24H, SCH$_2$CH$_2$), 3.62 – 3.44 (m, 288H, SCH$_2$CH$_2$O(CH$_2$CH$_2$O)$_6$), 3.30 – 3.28 (m, 36H, (CH$_2$CH$_2$O)$_6$CH$_3$), 3.14 (t, 24H, SCH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.3. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -136.4 – -136.5 (m, 24F, -meta), -145.3 (m, 24F, -ortho). HRMS (Q-Exactive Plus): m/z calculated for C$_{336}$H$_{444}$B$_{12}$F$_{48}$O$_{96}$S$_{12}$ (M$^2$), 3721.3430 Da; found, 3721.3395 Da.

**Synthesis of 3j**

![3j structure](image)

3 (10.0 mg, 0.0029 mmol) and K$_2$PO$_4$ (32.0 mg, 0.151 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by mPEGthiol$_{766}$ (44.1 µL, 0.063 mmol). The vial was sealed again and set to stir at 400
rpm for 4 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex LH20 medium in MeOH (23 cm packed height), and the crude product mixture containing 3j was loaded onto the column with MeOH. 15 1-2 mL fractions were collected, dried via rotary evaporation, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via rotary evaporation to obtain an isolated yield of 7.7 mg (21 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 7.57 – 7.55 (br m, 24H, OCH$_2$-Ar), 7.18 – 7.16 (br m, 24H, OCH$_2$-Ar), 5.67 – 5.62 (br m, 24H, OCH$_3$), 3.72 (t, 24H, SCH$_2$CH$_2$), 3.64 – 3.51 (m, 744H, SCH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{15}$), 3.33 (m, 36H, (CH$_2$CH$_2$O)$_{15}$CH$_3$), 3.19 – 3.16 (t, 24H, SCH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.3. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -136.1 – -136.4 (m, 24F, -meta), -145.1 (m, 24F, -ortho).

**Synthesis of 3k**

![Structure of 3k](image)

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (27.0 mg, 0.127 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by mPEGthiol$_{2000}$ (85.0 mg, 0.043 mmol). The vial was sealed again and set to stir at 400 rpm for 20 hours. The vial was transferred out of the glovebox, and its contents were transferred
into an NMR tube for in situ $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and in situ $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. A 1.25 cm x 35 cm glass column was packed with Sephadex G50 medium in water (23 cm packed height), and the crude product mixture containing 3k was loaded onto the column with water. 15 1-2 mL fractions were collected, dried via lyophilization, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. The pure product fractions as indicated by NMR spectroscopy were combined and dried via lyophilization to obtain an isolated yield of 43.2 mg (54 %). $^1$H NMR (400 MHz, CD$_3$OD): δ 7.64 – 7.47 (br m, 24H, OCH$_2$-Ar), 7.20 (br m, 24H, OCH$_2$-Ar), 5.66 (br m, 24H, OCH$_2$), 3.92 – 3.44 (m, 2100H, SCH$_2$CH$_2$(CONH)CH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{42}$), 3.35 (s, 36H, (CH$_2$CH$_2$O)$_{42}$CH$_3$), 3.19 (t, 24H, SCH$_2$-CH$_2$). $^{11}$B NMR (128 MHz, CD$_3$OD): δ -15.4. $^{19}$F NMR (376 MHz, CD$_3$OD): δ -136.2 – -137.3 (m, 24F, -meta), -145.0 – -145.5 (m, 24F, -ortho). GPC trace of 3k measured in water with 0.02% NaN$_3$ at 12 °C gives a Đ (polydispersity index) of 1.081 (see Fig. 3c in main text).

**Synthesis of 3l**

![Structural formula of 3l](image)

3 (10.0 mg, 0.0029 mmol) and K$_3$PO$_4$ (18.7 mg, 0.088 mmol) were added along with a flea micro stir bar to a 4-mL glass vial, which was then sealed with a PTFE/silicone cap under ambient conditions. The vial was then purged and backfilled with N$_2$ three times before being transferred into the glovebox. In the glovebox, the vial was opened and 300 µL anhydrous DMF was added, followed by 1-thio-β-D-glucose tetraacetate (16.4 mg, 0.045 mmol). The vial was sealed again and...
set to stir at 400 rpm for 5 hours. The vial was transferred out of the glovebox, and its contents were transferred into an NMR tube for *in situ* $^{19}$F NMR spectroscopy to ensure nearly quantitative conversion and *in situ* $^{11}$B NMR spectroscopy to ensure structural integrity of the cluster. The crude mixture was then transferred into a 20-mL glass vial and lyophilized for solvent removal. The resulting residue was treated with NaOMe (3.8 mg, 0.07 mmol) in 1 mL MeOH for 2 hours. The volatiles were removed via rotary evaporation. The crude product mixture containing 3l was dissolved in water and adjusted to pH 7.3 using 3M HCl. This mixture was then centrifuged 5 times – after each of the first 4 centrifugation periods, the supernatant was removed by pipet and more water was added, after the 5th centrifugation period, the supernatant was removed and the precipitate was dried via lyophilization, and subjected to characterization via $^1$H, $^{11}$B, and $^{19}$F NMR spectroscopy. This pure product as indicated by NMR spectroscopy was dried via lyophilization to obtain an isolated yield of 5.3 mg (32 %). $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 7.62 – 7.46 (br m, 24H, OCH$_2$-Ar), 7.27 – 7.17 (br m, 24H, OCH$_2$-Ar), 5.65 – 5.56 (br m, 24H, OCH$_2$), 3.77 – 3.33, 3.28 (m, 84H, SCHCH$_2$OH(CHOH)$_3$CHO). $^{11}$B NMR (128 MHz, CD$_3$OD): $\delta$ -15.4. $^{19}$F NMR (376 MHz, CD$_3$OD): $\delta$ -135.4 – -135.5 (m, 24F, -meta), -145.5 – -145.6 (m, 24F, -ortho). HRMS (Q-Exactive Plus): $m/z$ calculated for C$_{228}$H$_{204}$B$_{12}$F$_{48}$O$_{72}$S$_{12}$ (M$^+$), 1840.3100 Da; found, 1840.3178 Da.
$^{13}$C{$^1$H} NMR

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EXPNO  10
PROCNO  1

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PLW3  0.106000000 W

F2 - Processing parameters
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$^{19}$F NMR

Current Data Parameters
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PROCNO 1

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D1      2.00000000 sec
TD0     1

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PLW1    17.00000000 W

F2 - Processing parameters
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SSB     0
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PC      1.00
$^{13}\text{C}\{^1\text{H}\}$ NMR
$^{19}$F NMR

Current Data Parameters
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PROCNO 1

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SWH     150000.000 Hz
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RG      189.85
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DE      6.50 usec
TE      290.0 K
D1      2.000000000 sec
TD0     1

--------------- CHANNEL f1 ---------------
SFO1    376.4983660 MHz
NUC1    19F
PJ      14.50 usec
PLW1    17.00000000 W

F2 - Processing parameters
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PC      1.00
$^1$H NMR

Current Data Parameters
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EXPNO 91
PROCNO 1

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TE 299.0 K
D1 2.0000000 sec
TD0 1

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PLW1 13.00000000 W

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SSB 0
LB 0.30 Hz
GB 0
PC 1.00
$^{19}F$ NMR
Q Exactive High-Res Mass Spec

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m/z 1703.7786
m/z 1794.7544
m/z 3407.5278
Q Exactive
High-Res Mass Spec

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in situ $^{11}$B NMR

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EXPNO 31
PROCNO 1

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RG 189.85
DW 9.800 usec
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TE 290.0 K
D1 0.05000000 sec
TD0 1

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NUC1 11B
PI 10.00 usec
PLW1 52.00000000 W

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$^{11}$B $\{^1$H$\}$ NMR

Current Data Parameters
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PROCNO 1

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DW 9.800 usec
TE 299.1 K
D1 0.05000000 sec
D11 0.05000000 sec
TDD 1

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NUC1 1H
P1 10.00 usec
PW1 52.00000000 W

********** CHANNEL f2 **********
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PCPD2 90.00 usec
PLW1 13.00000000 W
PLW12 0.36110000 W

F2 - Processing parameters
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SF 128.3776161 MHz
WDW EM
SSB 0
LB 0
GB 10.00 Hz
PC 1.40

60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm
Small impurities are present due to the commercial 1-hexanethiol used (95% pure).
Waters Mass Spec

high m/z scan
2a 19 (1.060) Cm (9.36)

2-2[Et3NH]+

mass spec

1220.64
1370.60
1836.29
1835.25
1834.79
1837.79
3436.93
3439.92
3440.94
3636.66
3633.54
3634.54
3673.72
3677.73
3674.73
3676.73
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3699.84
3800.00
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4800.00

m/z
Waters
Mass Spec
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
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EXPNO  220
PROCNO  1

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PULPROG  zgflip30
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DE  6.50 usec
TE  290.0 K
D1  2.00000000 sec
TD0  1

--------------- CHANNEL f1 ---------------
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NUC1  19F
P1  14.50 usec
PLW1  17.00000000 W

F2 - Processing parameters
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SSB  0
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$1^\text{H} \text{NMR}$

Current Data Parameters
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EXPNO  102
PROCNO  1

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PULPROG  zg30
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\text{S}
\end{array} \]

\[ 11\text{B} \{^1\text{H}\} \text{ NMR} \]
$2 \cdot [\text{Et}_2\text{NH}]^+$

$\text{S}$

$\text{O}$

$\text{F}$

$\text{F}$

$\text{F}$

$\text{NMR}$

$^{19}\text{F}$

**Bruker**

Current Data Parameters
- **NAME**: Feb03-2016
- **EXPNO**: 101
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20160203
- **Time**: 15:10
- **INSTRUM**: av400
- **PROBHD**: 5 mm PABBO BB/
- **PULPROG**: zg30p30
- **TD**: 262144
- **SOLVENT**: CD3CN
- **NS**: 64
- **DS**: 0
- **SWH**: 1500000.000 Hz
- **FIDRES**: 0.572205 Hz
- **AQ**: 0.8736133 sec
- **RG**: 189.85
- **DW**: 3.333 ussec
- **DE**: 6.50 ussec
- **TE**: 299.0 K
- **D1**: 2.0000000 sec
- **TD0**: 1

**CHANNEL**
- **SFO1**: 376.4983660 MHz
- **NUC1**: 19F
- **P1**: 14.50 ussec
- **PLW1**: 17.0000000 W

**F2 - Processing parameters**
- **SI**: 262144
- **SF**: 376.4983660 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **GB**: 0
- **FC**: 1.00
Q Exactive
High-Res Mass Spec

2b 1.25-k #1-16  RT: 0.01-0.14  AV: 16  NL: 4.27E7
T: FTMS - p ESI Full ms [1250.00-4000.00]
in situ $^{11}$B NMR

Current Data Parameters
NAME 0201
EXPNO 131
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160201
Time 20.18
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 290.0 K
D1 0.05000000 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1 128.3776052 MHz
NUC1 11B
PI 10.00 usec
PLW1 52.0000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
in situ $^{19}$F NMR

Current Data Parameters
NAME  0201
EXPN0  130
PROCNO  1

F2 - Acquisition Parameters
Date_  20160201
Time  20.15
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflrp30
TD  262144
SOLVENT  None
NS  64
DS  0
SWH  150000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  290.0 K
D1  2.0000000 sec
TD0  1

------------- CHANNEL f1 --------------
SFO1  376.4983660 MHz
NUC1  19F
P1  14.50 usec
PLW1  17.0000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
\[ -2\cdot [\text{Et}_3\text{NH}]^+ \]

**1H NMR**

Current Data Parameters
NAME Feb03-2016
EXPNO 92
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160203
Time 14.59
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CD3CN
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2999060 sec
RG 155.85
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 5.00000000 sec
TD0 1

---------- CHANNEL f1 ----------
SF01 400.1324008 MHz
NUC1 H
PJ1 0.00000000 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
$^1\text{H}$ NMR
$^{19}$F NMR

Current Data Parameters
NAME Feb03-2016
EXPNO 91
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160203
Time 14.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg5p30
TD 262144
SOLVENT CD3CN
NS 64
DS 0
SWH 150000.00 Hz FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
TD0 1

---------- CHANNEL 1 ----------
SF01 376.4983660 MHz
NUC1 19F
PJ 14.50 usec
PLW1 17.00000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
Q Exactive
High-Res Mass Spec

2c 1-Sk #1-16  RT: 0.04-0.69  AV: 16  NL: 1.70E7
T: FTMS - p ESI Full ms [1000.00-5000.00]
Q Exactive
High-Res Mass Spec
in situ $^{11}$B NMR
in situ $^{19}$F NMR
$^1$H NMR

Current Data Parameters
NAME: G1 2ME 0204 0202 (MeOD)
EXPNO: 250
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160208
Time: 16.59
INSTRUM: av400
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 52882
SOLVENT: MeOD
NS: 32
DS: 0
SWH: 8012.820 Hz
FIDRES: 0.151523 Hz
AQ: 3.2998369 sec
RG: 155.85
DW: 62.400 usec
DE: 6.50 usec
TE: 299.0 K
D1: 5.00000000 sec
TD0: 1

-------------- CHANNEL f1 --------------
SFO1: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.00000000 W

F2 - Processing parameters
SI: 65536
SF: 400.1300078 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
$\overset{11}{\text{B}}$ NMR

Current Data Parameters
NAME    G1 2ME 0204 0202 (MeOD)
EXPNO   251
PROCNO  1

F2 - Acquisition Parameters
Date     20160208
Time    17.02
INSTRUM av400
PROBHD  5 mm PABBO BB/
PULPROG zg
TD      5096
SOLVENT MeOD
NS     1024
DS     0
SWH    51020.406 Hz
FIDRES 10.011854 Hz
AQ     0.0499408 sec
RG     189.85
DW     9.800 usec
DE     6.50 usec
TE     290.0 K
D1     0.0500000 sec
TD0    1

------------ CHANNEL f1 -------------
SF01    128.3776052 MHz
NUC1    11B
P1     10.00 usec
PLW1   52.0000000 W

F2 - Processing parameters
SI     32768
SF     128.3776161 MHz
WDW    EM
SSB    0
LB     10.00 Hz
GB     0
PC     1.40
$2^2 \ K^+$

$\text{SO}_3 \ F^-$

$\text{F} \ NMR$

Current Data Parameters
NAME    G1 2ME 0204 0202 (MeOD)
EXPNO   252
PROCNO  1

F2 - Acquisition Parameters
Date_   20160208
Time    17.06
INSTRUM av400
PROBHD  5 mm PABBO BB/
PULPROG zgflip30
TD      262144
SOLVENT MeOD
NS      64
DS      0
SWH     150000.000 Hz
FIDRES  0.572205 Hz
AQ      0.8738133 sec
RG      189.85
DW      3.333 usec
DE      6.50 usec
TE      290.0 K
D1      2.00000000 sec
TD0     1

阉----- CHANNEL f1 -----阉
SF01    376.4983660 MHz
NUC1    19F
P1      14.50 usec
PLW1    17.00000000 W

F2 - Processing parameters
SI      262144
SF      376.4983660 MHz
WDW     EM
SSB     0
LB      1.00 Hz
GB      0
PC      1.00
Q Exactive
High-Res Mass Spec
Q Exactive
High-Res Mass Spec

T: FTMS - p ESI Full ms [1000.00-4000.00]

m/z 1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603
Relative Abundance

1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603
m/z 1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603
Relative Abundance

1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603
m/z 1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603
Relative Abundance
in situ $^{11}$B NMR
in situ $^{19}$F NMR

**Current Data Parameters**
- **NAME**: 0203
- **EXPNO**: 50
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20160203
- **Time**: 13:22
- **INSTRUM**: av400
- **PROBHID**: 5 mm PABBO BB/
- **PULPROG**: zgflip30
- **TD**: 262144
- **SOLVENT**: None
- **NS**: 64
- **DS**: 0
- **SWH**: 150000.000 Hz
- **FIDRES**: 0.572205 Hz
- **AQ**: 0.8738133 sec
- **RG**: 189.85
- **DW**: 3.333 usec
- **DE**: 6.50 usec
- **TE**: 299.0 K
- **D1**: 2.00000000 sec
- **TD0**: 1

**SFO1**: 376.4983660 MHz
- **NUC1**: $^{19}$F
- **PI**: 14.50 usec
- **PLW1**: 17.00000000 W

**F2 - Processing parameters**
- **SI**: 262144
- **SF**: 376.4983660 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **GB**: 0
- **PC**: 1.00
$^{11}$B NMR

Current Data Parameters
NAME      G1 Glycerol 0204 0202 (MeOD)
EXPNO     91
PROCNO    1

F2 - Acquisition Parameters
Date_     20160205
Time      12.40
INSTRUM   av400
PROBHD    5 mm PABBO BB/
PULPROG   zg
TD        5096
SOLVENT   MeOD
NS        1024
DS        0
SWH       51020.406 Hz
FIDRES    10.011854 Hz
AQ        0.0499408 sec
RG        189.85
DW        9.800 usec
DE        6.50 usec
TE        299.0 K
D1        0.05000000 sec
TD0       1

MARYLAND CHANNEL f1
SFO1      128.3776052 MHz
NUC1      11B
PI        10.00 usec
PLW1      52.00000000 W

F2 - Processing parameters
SI        32768
SF        128.3776161 MHz
WDW       EM
SSB       0
LB        0
GB        10.00 Hz
PC        1.40

---
Q Exactive
High-Res Mass Spec

2e #1-10  RT: 0.01-0.09  AV: 10  NL: 1.77E8
T: FTMS - p ESI Full ms [400.00-6000.00]
in situ $^{11}$B NMR
in situ $^{19}\text{F} \text{NMR}$
$\text{SO}_3\text{NH}_2 \quad 2^-\ K^+$

$^{11}\text{B NMR}$

Current Data Parameters
NAME  G1 CA 0303 0224 (MeOD)
EXPNO  81
PROCNO  1

F2 - Acquisition Parameters
Date_  20160303
Time  20.09 h
INSTRUM  av-400
PROBHD  Z18618_0656 (zg
PULPROG  T0
TD  5096
SOLVENT  MeOD
NS  1024
DS  0
SW1  51020.406 Hz
FIDRES  20.023708 Hz
AQ  0.0499408 sec
RG  189.85
DW  9.800 usec
DE  6.50 usec
TE  299.0 K
D1  0.05=00000 sec
TD0  1
SFO1  128.3776052 MHz
NUC1  11B
P1  10.00 usec
PLW1  52.00000000 W

F2 - Processing parameters
SI  32768
SF  128.3776161 MHz
WDW  EM
SSB  0
LB  10.00 Hz
GB  0
PC  1.40
$\text{SOF}_2F_2\text{NH}_2$  \[ 2^2K^+ \]

$^{19}\text{F NMR}$

Current Data Parameters
NAME  G1 CA 0303 0224 (MeOD)
EXPNO  82
PROCNO  1

F2 - Acquisition Parameters
Date_  20160303
Time  20.14 h
INSTRUM  av-400
PROBHD  Z108618_0066 (ZGFLQ430)
PULPROG  262144
SOLVENT  MeOD
NS  64
DS  0
SW1  150000.000 Hz
FIDRES  1.144409 Hz
AQ  0.8738133 sec
RG  189.85
DW  1.333 ussec
DE  6.50 ussec
TE  299.0 K
D1  2000000 sec
TD0  1
SFO1  376.4983660 MHz
NUC1  19F
P1  14.50 ussec
PLW1  1700000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
NAME     0711
EXPNO    50
PROCNO   1

F2 - Acquisition Parameters
Date_    20160711
Time     18:23
INSTRUM  av400
PROBHD   5 mm PABBO BB/
PULPROG  zgflip30
TD       262144
SOLVENT  None
NS       64
DS       0
SWH      150000.000 Hz
FIDRES   0.572205 Hz
AQ       0.8738133 sec
RG       189.85
DW       3.333 usec
DE       6.50 usec
TE       299.0 K
D1       2.00000000 sec
TD0      1

--------------- CHANNEL f1 ---------------
SF01      376.4983660 MHz
NUC1      19F
P1        14.50 usec
PLW1      17.00000000 W

F2 - Processing parameters
SI        262144
SF        376.4983660 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.00
$^{1}H$ NMR
$^{11}$B NMR

Current Data Parameters
NAME: G1 PEG350 8 mg 0713 0710 (MeOD)
EXPNO: 30
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160713
Time: 14.52
INSTRUM: av400
PROBHD: 5 mm PABBO BB/
PULPROG: zg
TD: 5096
SOLVENT: MeOD
NS: 1024
DS: 0
SWH: 51020.406 Hz
FIDRES: 10.011854 Hz
AQ: 0.0499408 sec
RG: 489.85
DW: 9.800 usec
DE: 6.50 usec
TE: 299.0 K
D1: 0.05000000 sec
TDO: 1

====== CHANNEL (1) ======
SFO1: 128.3776052 MHz
NUC1: 11B
PI: 10.00 usec
PLW1: 52.00000000 W

F2 - Processing parameters
SI: 32768
SF: 128.3776161 MHz
WDW: EM
SSB: 0
LB: 10.00 Hz
GB: 0
PC: 1.40
$^{19}\text{F NMR}$

Current Data Parameters
- **NAME**: G1 PEG350.8 mg 0713 0710 (MeOD)
- **EXPNO**: 31
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20160713
- **Time**: 14:56
- **INSTRUM**: av400
- **PROPAB**: 5 mm PABBO BB/
- **PULPROG**: zgflp30
- **TD**: 262144
- **SOLVENT**: MeOD
- **NS**: 64
- **DS**: 0
- **SWH**: 150000.000 Hz
- **FIDRES**: 0.572205 Hz
- **AQ**: 0.8738133 sec
- **RG**: 189.85
- **DW**: 3.333 usec
- **DE**: 6.50 usec
- **TE**: 299.0 K
- **DI**: 2.0000000 sec
- **TD0**: 1

**CHANNEL f**
- **SFO1**: 376.4983660 MHz
- **NUC1**: 19F
- **F1**: 14.50 usec
- **PLW1**: 17.0000000 W

**F2 - Processing parameters**
- **SI**: 262144
- **SF**: 376.4983660 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **GB**: 0
- **PC**: 1.00
Q Exactive
High-Res Mass Spec

2i #1-16  RT: 0.01-0.14  AV: 16  NL: 2.75E6
T: FTMS - p ESI Full ms [400.00-6000.00]
Q Exactive High-Res Mass Spec

2i #1-16   RT: 0.01-0.14   AV: 16   NL: 2.75E6
T: FTMS - p ESI Full ms [400.00-6000.00]

O
CH₃

O
F
F
F
F

Q Exactive
High-Res Mass Spec

m/z

3261.1154
3262.0897
3263.1504
3264.6451
3266.1450
3266.6439
3267.1457
3268.1453
3269.1497
3270.1460
3270.6533
3271.1460

z=2
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$\text{Br}$\n
\begin{center}$\text{O} - \text{O} - \text{CH}_3$\end{center}

$^1\text{H NMR}$

---

**Current Data Parameters**
- **NAME**: mPEG-Br
- **EXPNO**: 60
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20151213
- **Time**: 15:05
- **INSTRUM**: av400
- **PROBHD**: 5 mm PABBO BB/
- **PULPROG**: zg30
- **TD**: 52882
- **SOLVENT**: CDCl3
- **DS**: 64
- **SWH**: 8012.820 Hz
- **FIDRES**: 0.151523 Hz
- **AQ**: 3.2908369 sec
- **RG**: 12.23
- **DW**: 62.400 usec
- **DE**: 6.50 usec
- **TE**: 290.0 K
- **D1**: 2.00000000 sec
- **TD0**: 1

---

**CHANNEL f1**
- **SF01**: 400.1324008 MHz
- **NUC1**: 1H
- **PJ**: 15.00 usec
- **PLW1**: 13.00000000 W

**F2 - Processing parameters**
- **SI**: 65536
- **SF**: 400.1300173 MHz
- **WDDW**: EM
- **SSB**: 0
- **LB**: 0.30 Hz
- **GB**: 0
- **PC**: 1.00
$^1$H NMR

Current Data Parameters
NAME mPEG-SAc
EXPNO 160
PROCNO 1

Date_ 20151215
Time 17.02

INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT CDCl3
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 73.86
DW 62.400 usec
DE 6.50 usec
TE 290.0 K
D1 2.00000000 sec
TD0 1

----------- CHANNEL f1 -----------
SF01 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300176 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
NAME 0209
EXPCNO 90
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160209
Time 19.24
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflqnp30
TD 262144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 290.0 K
D1 2.000000000 sec
TD0 1

=CHANNEL f1=
SFO1 376.4983660 MHz
NUC1 $^{19}$F
P1 14.50 usec
PLW1 17.0000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
* These peaks correspond to small impurities - boric acid and borates.
19F NMR
in situ $^{11}$B NMR

Current Data Parameters
NAME 0209
EXPNO 101
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160209
Time 19.36
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 290.0 K
D1 0.05000000 sec
TD0 1

CHANNEL f1
SFO1 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
in situ $^{19}$F NMR

Current Data Parameters
NAME 0209
EXPN0 100
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160209
Time 19.33
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zgflpq30
TD 162144
SOLVENT None
NS 64
DS 0
SWH 150000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.333 usec
DE 6.50 usec
TE 290.0 K
D1 2.000000000 sec
TD1 1

SFO1 376.4983660 MHz
NUC1 19F
PJ1 14.50 usec
PLW1 17.0000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
$\text{H NMR}$

Current Data Parameters
NAME  G1 PEG2000 0211 0208 MeOD
EXPNO   100
PROCNO  1

F2 - Acquisition Parameters
Date  20160216
Time  21.55
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD  52882
SOLVENT  MeOD
NS  32
DS  0
SWH  8012.820 Hz
FIDRES  0.151523 Hz
AQ  3.2990369 sec
RG  155.85
DW  62.400 usec
DE  6.50 usec
TE  299.0 K
D1  10.0000000 sec
TD0  1

======== CHANNEL f1 ========
SFO1  400.1324008 MHz
NUM1  11
P1  15.00 usec
PLW1  13.00000000 W

F2 - Processing parameters
SI  65536
SF  400.1300076 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

108
* These peaks correspond to small impurities - boric acid and borates.
in situ $^{11}$B NMR
Split peaks are due to the restricted rotational conformations of the molecule. \(^9\)
$^{1}H$ NMR

Current Data Parameters
NAME   G1 Gie 2 0711 0307 D2O
EXPNO   202
PROCNO   1

F2 - Acquisition Parameters
Date_  20160713
Time    20.32
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD     52882
SOLVENT D2O
NS     32
DS     6
SWH    8012.820 Hz
FIDRES  0.151523 Hz
AQ    3.2998369 sec
RG     189.85
DW     62.400 usec
DE     6.50 usec
TE    290.0 K
D1  5.000000000 sec
TD0   1

========== CHANNEL f1 ==========
SFO1  400.1324008 MHz
NUC1   1H
P1   15.00 usec
PLW1  13.00000000 W

F2 - Processing parameters
SI    65536
SF   400.1299638 MHz
WDW  EM
SSB  0
LB    0.30 Hz
GB  0
PC    1.00
$\text{SO}_1$  $2\text{K}^+/\text{Na}^+$

$\text{11}^B\text{ NMR}$

Bruker

Current Data Parameters
NAME   G1 Glc 2 0711 0307 D2O
EXPNO   200
PROCNO   1

F2 - Acquisition Parameters
Date_   20160713
Time   20.23
INSTRUM   av400
PROBHD   5 mm PABBO BB/
PULPROG   zg
TD   5096
SOLVENT   D2O
NS   1024
DS   0
SWH   51020.406 Hz
FIDRES   10.011854 Hz
AQ   0.0499408 sec
RG   189.85
DW   9.800 usec
DE   6.50 usec
TE   299.0 K
D1   0.05000000 sec
TD0   1

------------- CHANNEL f1 -------------
SFO1   128.3776052 MHz
NUC1   11B
P1   10.00 usec
PLW1   52.0000000 W

F2 - Processing parameters
SI   32768
SF   128.3776161 MHz
WDM   EM
SSB   0
LB   10.00 Hz
GB   0
PC   1.40
$^{19}$F NMR

Broad, split peaks are due to the restricted rotational conformations of the molecule.\textsuperscript{9}
Q Exactive
High-Res Mass Spec
Q Exactive
High-Res Mass Spec
"in situ\textsuperscript{11}B NMR"
Small impurities are present due to the commercial 1-hexanethiol used (95% pure).
$2\cdot 2[\text{Et}_3\text{NH}]^+$

$\text{OS}_12$ $\text{FF}$ $\text{FF}$ $\text{N}$

$\text{H NMR}$

Current Data Parameters
NAME: Jan26-2016
EXPNO: 41
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160126
Time: 13.00
INSTRUM: av400
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 128204
SOLVENT: CD3CN
NS: 32
DS: 0
SWH: 8012.820 Hz
FIDRES: 0.062501 Hz
AQ: 7.9999294 sec
RG: 155.85
DW: 62.400 usec
DE: 6.50 usec
TE: 290.0 K
D1: 5.0000000 sec
TD0: 1

---------- CHANNEL [1] ----------
SFO1: 400.1324008 MHz
NUC1: H
PJ: 15.00 usec
PLW1: 13.00000000 W

F2 - Processing parameters
SI: 65536
SF: 400.1300114 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
$^{11}\text{B} \{^1\text{H}\} \text{ NMR}$

Current Data Parameters
NAME     Jan26-2016
EXPN0    46
PROCNO   1

F2 - Acquisition Parameters
Date_     20160126
Time_     12.53
INSTRUM   zv400
PROHID    5 mm PABBO BB/
PULPROG   zgdc.js
TD        5066
SOLVENT   CD3CN
N5        1024
DS        0
SW1H      51020.406 Hz
FIDRES    10.0111854 Hz
AQ        0.0494908 sec
RG        189.85
DW        9.800 usec
TE        299.1 K
D1        0.05000000 sec
D11       0.03000000 sec
TD0       1

********* CHANNEL f1 *********
SF01      128.377652 MHz
NUC1      H
P1        10.00 usec
PL,W1     52.00000000 W

********* CHANNEL f2 *********
SF02      400.1324808 MHz
NUC2      H
CPDPROG   1 wait16
PCPF32    90.00 usec
PL,W2     13.00000000 W
PL,W12    0.36110000 W

F2 - Processing parameters
ST        32768
SF        128.3776161 MHz
WDW       EM
SSB       0
LB        10.00 Hz
GB        0
PC        1.40
Small impurities are present due to the commercial 1-hexanethiol used (95% pure).
Q Exactive
High-Res Mass Spec
Q Exactive
High-Res Mass Spec
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
NAME  0119
EXPNO  130
PROCNO  1

F2 - Acquisition Parameters
Date_  20160119
Time  19.35
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflpq30
TD  262144
SOLVENT  None
NS  64
DS  0
SWH  150000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  299.0 K
D1  2.0000000 sec
TD0  1

----------- CHANNEL f1 -----------
SF01  376.4983660 MHz
NUC1  19F
PJ  14.50 usec
PLW1  17.0000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
$^{11}$B $\{^1$H$\}$ NMR
$2-2[\text{Et}_2\text{NH}]^+$

$^{19}\text{F NMR}$

Current Data Parameters
NAME: Jan22-2016
EXPNO: 72
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160122
Time: 15.17
INSTRUM: av400
PROBHD: 5 mm PABBO B/B
PULPROG: zgRpr30
TD: 262144
SOLVENT: CD3CN
NS: 64
DS: 0
SWH: 150000.000 Hz
FIDRES: 0.572205 Hz
AQ: 0.8738133 sec
RG: 189.85
DW: 3.333 uscc
DE: 6.50 uscc
TE: 299.0 K
D1: 2.00000000 sec
TD0: 1

--------------- CHANNEL 1 -----------------
SFO1: 376.4983660 MHz
NUC1: 19F
PJ: 14.50 uscc
PLW1: 17.0000000 W

F2 - Processing parameters
SI: 262144
SF: 376.4983660 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.00
Q Exactive
High-Res Mass Spec
Q Exactive
High-Res Mass Spec

3b 1-4k #1-19  RT: 0.01-0.16  AV: 19  NL: 1.40E7
T: FTMS - p ESI Full ms [1000.00-4000.00]
in situ $^{11}$B NMR

Current Data Parameters
NAME 0120
EXPNO 71
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160120
Time 18.53
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 290.0 K
D1 0.050000000 sec
TD0 1

====== CHANNEL f1 ======
SF01 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
in situ $^{19}$F NMR
2-2[Et₂NH]⁺

$\text{SOF}_4$

$\text{H NMR}$

Current Data Parameters
NAME: Jan26-2016
EXPNO: 31
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160126
Time: 12:36
INSTRUM: av400
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 128204
SOLVENT: CD3CN
NS: 32
DS: 0
SWH: 8012.820 Hz
FIDRES: 0.062501 Hz
AQ: 7.99999294 sec
RG: 155.85
DW: 62.400 usec
DE: 6.50 usec
TE: 299.0 K
D1: 5.00000000 sec
TD0: 1

---------- CHANNEL 1 ----------
SF01: 400.1324008 MHz
NUC1: 1H
PJ1: 15.00 usec
PLW1: 13.00000000 W

F2 - Processing parameters
SI: 65536
SF: 400.1300113 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
$^{11}\text{B} \{^1\text{H}\} \text{ NMR}$
$2-2\text{[Et₃NH]}^+$

**F NMR**

Current Data Parameters
NAME Jan26-2016
EXPNO 32
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160126
Time 12.40
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg3qpr30
TD 262144
SOLVENT CD3CN
NS 6
DS 0
SWH 15000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8736133 sec
RG 189.85
DW 3.333 ussec
DE 6.50 ussec
TE 299.0 K
D1 2.0000000 sec
TD0 1

************ CHANNEL [f] ************
SFO1 376.4983660 MHz
NUC1 19F
PJ 14.50 ussec
PLW1 17.0000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
Q Exactive
High-Res Mass Spec

3c #1-16  RT: 0.01-0.14  AV: 16  NL: 1.92E6
T: FTMS - p ESI Full ms [400.00-6000.00]
Q Exactive
High-Res Mass Spec

3c #1:16  RT: 0.01-0.14  AV: 16  NL: 1.92E6
T: FTMS - p ESI Full ms [400.00-6000.00]
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
NAME  0110
EXPNO  40
PROCNO  1

F2 - Acquisition Parameters
Date_  20160110
Time  20.34
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflpq30
TD  262144
SOLVENT  None
NS  64
DS  6
SWH  150000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  299.0 K
D1  2.00000000 sec
TD0  1

======== CHANNEL f1 ========
SFO1  376.4983660 MHz
NUC1  19F
P1  14.50 usec
PLW1  17.0000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
$^{1}H$ NMR

Current Data Parameters
NAME: G2 2ME 0111 0110 (MeOD)
EXPNO: 1160
PROCNO: 1

F2 - Acquisition Parameters
Date: 20160112
Time: 16:27
INSTRUM: av400
PROBH: 5 mm PABBO BB/
PULPROG: zg30
TD: 52882
SOLVENT: MeOD
NS: 32
DS: 6
SWH: 8012.820 Hz
FIDRES: 0.151523 Hz
AQ: 3.29098369 sec
RG: 155.85
DW: 62.400 usec
DE: 6.50 usec
TE: 299.0 K
D1: 2.00000000 sec
TD0: 1

---------- CHANNEL f1 ----------
SF01: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.00000000 W

F2 - Processing parameters
SI: 65536
SF: 400.1300078 MHz
WIDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
$^{11}\text{B NMR}$

Current Data Parameters
NAME  G2 2ME 0111 0110 (MeOD)
EXPNO  1162
PROCNO  1

F2 - Acquisition Parameters
Date_  20160112
Time  16.35
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zg
TD  5096
SOLVENT  MeOD
NS  1024
DS  0
SWH  51020.406 Hz
FIDRES  10.011854 Hz
AQ  0.0499408 sec
RG  189.85
DW  9.800 usec
DE  6.50 usec
TE  290.0 K
DI  0.0500000 sec
TD0  1

--------------- CHANNEL f1 -------------
SFO1  128.3776052 MHz
NUC1  11B
PJ  10.00 usec
PLW1  52.0000000 W

F2 - Processing parameters
SI  32768
SF  128.3776161 MHz
WDW  EM
SSB  0
LB  10.00 Hz
GB  0
PC  1.40
$^{19}\text{F NMR}$

**Current Data Parameters**
- NAME: G22ME01110110 (MeOD)
- EXPNO: 1161
- PROCNO: 1

**F2 - Acquisition Parameters**
- Date: 20160112
- Time: 16.32
- INSTRUM: av400
- PROBHD: 5 mm PABBO BB/
- PULPROG: zgflgp30
- TD: 262144
- SOLVENT: MeOD
- NS: 64
- DS: 0
- SWH: 150000.000 Hz
- FIDRES: 0.572205 Hz
- AQ: 0.8738133 sec
- RG: 189.85
- DW: 3.333 usec
- DE: 6.500 usec
- TE: 290.0 K
- D1: 2.00000000 sec
- TD0: 1

**F2 - Processing parameters**
- SI: 262144
- SF: 376.4983660 MHz
- WDW: EM
- SSBI: 0
- LB: 1.00 Hz
- GB: 0
- PC: 1.00
Q Exactive
High-Res Mass Spec
in situ $^{11}$B NMR

Current Data Parameters
NAME 0110
EXPNO 61
PROCNO 1

F2 - Acquisition Parameters
Date 20160110
Time 20.56
INSTRUM av400
PROBHDX 5 mm PABBO BB
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH 51020.406 Hz
FIDRES 10.011854 Hz
AQ 0.0499408 sec
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 290.0 K
D1 0.05000000 sec
TD0 1

--------------- CHANNEL f1 ---------------
SF01 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDM EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
in situ $^{19}$F NMR

Current Data Parameters
NAME  0110
EXPNO  60
PROCNO  1

F2 - Acquisition Parameters
Date_  20160110
Time  20.53
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflsp30
TD  262144
SOLVENT  None
NS  64
DS  0
SWH  150000.000 Hz
FIDRES  0.5772205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  299.0 K
D1  2.00000000 sec
TD0  1

CHANNEL f1
SFO1  376.4983660 MHz
NUC1  19F
PJ  14.50 usec
PLW1  17.00000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
`OH

`OH

F  

F

F

12

\[ \text{H NMR} \]

Current Data Parameters
NAME  G2 Glycerol 0111 0110 (MeOD)
EXPNO  250
PROCNO  1

F2 - Acquisition Parameters
Date  20160112
Time  22:11
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zg30
TD  52882
SOLVENT  MeOD
NS  32
DS  6
SWH  8012.820 Hz
FIDRES  0.151523 Hz
AQ  3.2998369 sec
RG  155.85
DW  62.400 usec
DE  6.50 usec
TE  290.0 K
D1  2.00000000 sec
TD0  1

---------- CHANNEL f1 ----------
SFO1  400.1324008 MHz
NUC1  1H
PJ  15.00 usec
PLW1  13.00000000 W

F2 - Processing parameters
SI  65536
SF  400.1300077 MHz
WDM  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
$\text{19F NMR}$

Current Data Parameters
NAME  G2 Glycerol 0111 0110 (MeOD)
EXPNO  251
PROCNO  1

F2 - Acquisition Parameters
Date_  20160112
Time  22:15
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflqpx30
TD  262144
SOLVENT  MeOD
NS  64
DS  0
SWH  15000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  290.0 K
D1  2.0000000 sec
TD0  1

--------------- CHANNEL f1 ---------------
SFO1  376.4983660 MHz
NUC1  19F
PJ  14.50 usec
PLW1  17.0000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
Q Exactive
High-Res Mass Spec
Q Exactive
High-Res Mass Spec

m/z

2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238

Relative Abundance

2232.8740 $z=2$
2232.3752 $z=2$
2231.8746 $z=2$
2233.3729 $z=2$
2233.8731 $z=2$
2231.3736 $z=2$
2234.3739 $z=2$
2230.8750 $z=2$

FTMS - p ESI Full ms [400.00-6000.00]
in situ $^{11}$B NMR
in situ $^{19}\text{F} \text{NMR}$
$^{1}H$ NMR

Current Data Parameters
NAME  G2 CA 0112 0110 (ACN & MeOD)
EXPTNO  3
PROCNO  1

F2 - Acquisition Parameters
Date_  20160113
Time  19.32
INSTRUM  av300
PROBHD  5 mm PABBO BB-
PULPROG  zg30
TD  65536
SOLVENT  CD3CN
NS  32
DS  0
SWH  5995.204 Hz
FIDRES  0.091480 Hz
AQ  5.4657025 sec
RG  574.7
DW  83.400 ussec
DE  6.00 ussec
TE  297.8 K
D1  2.0000000 sec
TD0  1

---------- CHANNEL f1 ----------
NUC1  1H
P1  14.75 ussec
PL1  0 dB
PL1W  9.31909847 W
SF01  300.1318008 MHz

F2 - Processing parameters
SI  65536
SF  300.1300074 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.40
Waters
Mass Spec
Waters
Mass Spec
in situ $^{11}$B NMR

**Current Data Parameters**
- **NAME**: 0623
- **EXPNO**: 91
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20160623
- **Time**: 19.12
- **INSTRUM**: av400
- **PROBHD**: 5 mm PABBO BB/
- **PULPROG**: zg
- **TD**: 5096
- **SOLVENT**: None
- **NS**: 1024
- **DS**: 0
- **SWH**: 51020.406 Hz
- **FIDRES**: 10.011854 Hz
- **AQ**: 0.0499408 sec
- **RG**: 189.85
- **DW**: 9.800 usec
- **DE**: 6.50 usec
- **TE**: 290.0 K
- **D1**: 0.05000000 sec
- **TD0**: 1

**CHANNEL f1**
- **SF01**: 128.3776502 MHz
- **NUC1**: 11B
- **P1**: 10.00 usec
- **PLW1**: 52.00000000 W

**F2 - Processing parameters**
- **SI**: 32768
- **SF**: 128.3776161 MHz
- **WDW**: EM
- **SSB**: 0
- **LB**: 10.00 Hz
- **GB**: 0
- **PC**: 1.40
in situ $^{19}$F NMR
$^{11}$B NMR

Current Data Parameters
NAME  G2 BC 0630 0623 (MeOD)
EXPNO  52
PROCNO  1

F2 - Acquisition Parameters
Date_ 20160630
Time  19.54
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD  5096
SOLVENT MeOD
NS  1024
DS  0
SWH  51020.406 Hz
FIDRES  10.011854 Hz
AQ  0.0499408 sec
RG  189.85
DW  9.800 usec
DE  6.500 usec
TE  290.0 K
D1  0.05000000 sec
TD0  1

========== CHANNEL f1 ==========
SF01  128.3776052 MHz
NUC1  11B
P1  10.00 usec
PLW1  52.00000000 W

F2 - Processing parameters
SI  32768
SF  128.3776161 MHz
WDM  EM
SSB  0
LB  10.00 Hz
GB  0
PC  1.40
in situ $^{11}$B NMR
in situ $^{19}$F NMR

Current Data Parameters
NAME 0520
EXPN0 130
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160520
Time 21.10
INSTRUM av400
PROBH D 5 mm PABBO BB/
PULPROG zgflk,30
TD 262.44
SOLVENT None
NS 64
DS 0
SWH 15000.000 Hz
FIDRES 0.572205 Hz
AQ 0.8738133 sec
RG 189.85
DW 3.303 usc
DE 6.50 usec
TE 290.0 K
D1 2.0000000 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1 376.4983660 MHz
NUC1 19F
PJ1 14.50 usec
PLW1 17.0000000 W

F2 - Processing parameters
SI 262144
SF 376.4983660 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
* This peak corresponds to a small boric acid impurity.
$^{19}$F NMR

Current Data Parameters
NAME   G2 CAG 0620 0520 (ACN & D2O)
EXPNO   81
PROCNO  1

F2 - Acquisition Parameters
Datec.  20160622
Time    16.22
INSTRUM av400
PROBHLD 5 mm FABBO BB/
PULPROG zgflq30
TD      262144
SOLVENT CD3CN
NS      64
DS      0
SWH     150000.000 Hz
FIDRES  0.572205 Hz
AQ      0.8738133 sec
RG      189.85
DW      3.333 usec
DE      6.50 usec
TE      299.0 K
D1      2.000000000 sec
TD0     1

CHANNEL 1
SFO1   376.4983660 MHz
NUC1   19F
P1     14.50 usec
PLW1   17.0000000 W

F2 - Processing parameters
SI     262144
SF     376.4975772 MHz
WDW    EM
SSB    0
LIR    1.00 Hz
GIB    0
PC     1.00
G2 CAG 5 mg/mL, 4:1 H2O:MeCN
3h 145 (4.891)

Waters Mass Spec

2 TOF MS ES-
Waters
Mass Spec

G2 CAG 5 mg/mL, 4:1 H2O:MeCN
3h 145 (4.891)

2 TOF MS ES- 93.5
in situ $^{11}$B NMR

Current Data Parameters
NAME 1209
EXPNO 111
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151209
Time 20.03
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 5096
SOLVENT None
NS 1024
DS 0
SWH $51020.406 \, \text{Hz}$
FIDRES $10.011854 \, \text{Hz}$
AQ $0.0499408 \, \text{sec}$
RG 189.85
DW 9.800 usec
DE 6.50 usec
TE 290.0 K
D1 $0.05000000 \, \text{sec}$
TD0 1

------------- CHANNEL f1 --------------
SF01 128.3776052 MHz
NUC1 11B
P1 10.00 usec
PLW1 52.00000000 W

F2 - Processing parameters
SI 32768
SF 128.3776161 MHz
WDW EM
SSB 0
LB 10.00 Hz
GB 0
PC 1.40
**in situ** $^{19}$F NMR

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**Current Data Parameters**

| Parameter   | Value                  |
|-------------|------------------------|
| NAME        | 1209                   |
| EXPNO       | 110                    |
| PROCNO      | 1                      |

**F2 - Acquisition Parameters**

- Date: 2015-12-09
- Time: 20:00
- INSTRUM: av400
- PROBHD: 5 mm PABBO BB/
- PULPROG: zgflqns30
- TD: 262144
- SOLVENT: None
- NS: 64
- DS: 0
- SWH: 150000.00 Hz
- FIDRES: 0.572205 Hz
- AQ: 0.8738133 sec
- RG: 189.85
- DW: 3.333 usec
- DE: 6.50 usec
- TE: 299.0 K
- D1: 2.00000000 sec
- TD0: 1

**---------- CHANNEL f1 ----------**

- SF01: 376.4983660 MHz
- NUC1: 19F
- PI: 14.50 usec
- PLW1: 17.000000 W

**F2 - Processing parameters**

- SI: 262144
- SF: 376.4983660 MHz
- WDW: EM
- SSB: 0
- LB: 1.00 Hz
- GB: 0
- PC: 1.00
$^{19}$F NMR

Current Data Parameters
NAME  G2 PEG350 1217 1209 (MeOD)
EXPNO  4
PROCNO  1

F2 - Acquisition Parameters
Date_  20151220
Time  13.19
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflkp30
TD  262144
SOLVENT  MeOD
NS  64
DS  0
SWH  150000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  299.0 K
DI  2.00000000 sec
TD0  1

---------- CHANNEL f1 ----------
SFO1  376.4983660 MHz
NUC1  19F
P1  14.50 usec
PLW1  17.00000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
Q Exactive
High-Res Mass Spec

3i 2 #1-20 RT: 0.01-0.17 AV: 20 NL: 2.87E5
T: FTMS - p ESI Full ms [2000.00-6000.00]
Q Exactive
High-Res Mass Spec
in situ $^{11}$B NMR

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Current Data Parameters
NAME  0115
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20160115
Time  20.01
INSTRUM  av300
PROBHD  5 mm PABBO BB-
PULPROG  zg
TD  3848
SOLVENT  C6D6
NS  1024
DS  0
SWH  38535.645 Hz
FIDRES  10.014461 Hz
AQ  0.0499278 sec
RG  114
DW  12.975 usec
DE  6.00 usec
TE  297.7 K
D1  0.00000400 sec
TD0  1

---------- CHANNEL f1 ----------
NUC1  $^{11}$B
P1  5.00 usec
PL1  -2.00 dB
SF01  96.2936310 MHz

F2 - Processing parameters
SI  32768
SF  96.2935644 MHz
WDW  EM
SSB  0
LB  50.00 Hz
GB  0
PC  1.40
in situ $^{19}$F NMR
$^{1}H$ NMR

Current Data Parameters
NAME G2 PEG750 (MeOD)
EXPNO 160
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160119
Time 20.06
INSTRUM av400
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 52882
SOLVENT MeOD
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.151523 Hz
AQ 3.2998369 sec
RG 83.63
DW 62.400 usec
DE 6.50 usec
TE 299.0 K
D1 4.00000000 sec
TD0 1

--------------- CHANNEL f1 ---------------
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
$^{19}$F NMR

Current Data Parameters
NAME    G2PEG750 (MeOD)
EXPNO    162
PROCNO   1

F2 - Acquisition Parameters
Date_    20160119
Time     20.13
INSTRUM  av400
PROBHD   5 mm PABBO BB/
PULPROG  zgflgn30
TD       2621.44
SOLVENT  MeOD
NS       64
DS       0
SWH      150000.000 Hz
FIDRES   0.572205 Hz
AQ       0.8738133 sec
RG       189.85
DW       3.333 usec
DE       6.50 usec
TE       290.0 K
D1       2.00000000 sec
TD0      1

------------- CHANNEL f1 -------------
SFO1     376.4983660 MHz
NUC1     19F
PJ1      14.50 usec
PLW1     17.00000000 W

F2 - Processing parameters
SI       262144
SF       376.4983660 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00
in situ $^{11}$B NMR
in situ $^{19}$F NMR

**Current Data Parameters**
- **NAME**: 0126
- **EXPNO**: 80
- **PROCNO**: 1

**F2 - Acquisition Parameters**
- **Date**: 20160126
- **Time**: 16.27
- **INSTRUM**: av400
- **PROBHD**: 5 mm PABBO BB/
- **PULPROG**: zgflnp30
- **TD**: 262144
- **SOLVENT**: None
- **NS**: 64
- **DS**: 0
- **SWH**: 150000.000 Hz
- **FIDRES**: 0.572205 Hz
- **AQ**: 0.8738133 sec
- **RG**: 189.85
- **DW**: 3.333 usec
- **DE**: 6.50 usec
- **TE**: 290.0 K
- **D1**: 2.00000000 sec
- **TD0**: 1

**---------- CHANNEL f1 ----------**
- **SFO1**: 376.4983660 MHz
- **NUC1**: 19F
- **PI**: 14.50 usec
- **PLW1**: 17.0000000 W

**F2 - Processing parameters**
- **SI**: 262144
- **SF**: 376.4983660 MHz
- **WDD**: EM
- **SSB**: 0
- **LB**: 1.00 Hz
- **GB**: 0
- **PC**: 1.00
* This peak corresponds to a small boric acid impurity.
$^{19}$F NMR

Current Data Parameters
NAME  G2 PEG2000 0203 0125 MeOD
EXPNO  11
PROCNO  1

F2 - Acquisition Parameters
Date_  20160204
Time  17.15
INSTRUM  av400
PROBHD  5 mm PABBO BB/
PULPROG  zgflwp30
TD  262144
SOLVENT  MeOD
NS  64
DS  0
SWH  150000.000 Hz
FIDRES  0.572205 Hz
AQ  0.8738133 sec
RG  189.85
DW  3.333 usec
DE  6.50 usec
TE  299.0 K
D1  2.000000000 sec
TD0  1

============= CHANNEL f1 =============
SFO1  376.4983660 MHz
NUC1  19F
PJ  14.50 usec
PLW1  17.0000000 W

F2 - Processing parameters
SI  262144
SF  376.4983660 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.00
in situ $^{11}$B NMR
in situ $^{19}$F NMR
Q Exactive
High-Res Mass Spec
2D DOSY $^1$H NMR
2D DOSY $^1$H NMR
2D DOSY $^1$H NMR

Bruker
2D DOSY $^1$H NMR

2D DOSY
2D DOSY \textsuperscript{1}H NMR

![2D DOSY spectrum](image)
2D DOSY $^1$H NMR
Stability studies of 2i under biologically relevant conditions

Cell culture media/fetal bovine serum: 14.8 mg of 2i was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of serum media (440 μL cell culture media and 60 μL fetal bovine serum). This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by $^{11}$B and $^{19}$F NMR spectroscopy. This sample was then incubated at 37 °C for an additional 5 days and subjected to analysis via $^{11}$B and $^{19}$F NMR spectroscopy. No significant change was observed by NMR spectroscopy.

pH 5: 14.8 mg of 2i was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M citric acid/sodium citrate buffer at pH 5.0. This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by $^{11}$B and $^{19}$F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to boric acid and borates by $^{11}$B NMR spectroscopy as well as some peak broadening in $^{11}$B and $^{19}$F NMR spectra due to the oxidation of 2i from the 2- to the 1- oxidation state over time.

pH 7: 14.8 mg of 2i was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M Tris/HCl buffer at pH 7.0. This mixture was vortexed and then transferred to an NMR tube and monitored over 5 days at room temperature by $^{11}$B and $^{19}$F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to boric acid and borates by $^{11}$B NMR spectroscopy as well as some peak broadening in $^{11}$B and $^{19}$F NMR spectra due to the oxidation of 2i from the 2- to the 1- oxidation state over time.

pH 9: 14.8 mg of 2i was dissolved in 500 μL of Milli-Q water. 100 μL of this solution was added to 500 μL of a 0.1 M Tris/HCl buffer at pH 9.0. This mixture was vortexed and then transferred to
an NMR tube and monitored over 5 days at room temperature by $^{11}$B and $^{19}$F NMR spectroscopy. NMR spectroscopy suggests that the structural integrity is maintained. We note that we observed small impurities corresponding to borates by $^{11}$B NMR spectroscopy as well as some peak broadening in $^{11}$B and $^{19}$F NMR spectra due to the oxidation of 2i from the 2- to the 1- oxidation state over time.

**2-Mercaptoethanol:** 16.9 mg of 2i was dissolve in 2.82 mL of D$_2$O. 500 $\mu$L of this solution was added to 100 $\mu$L of a 120 mM 2-mercaptoethanol D$_2$O solution. This mixture was vortexed and then transferred to an NMR tube and monitored over 11 days at room temperature by $^1$H, $^{11}$B and $^{19}$F NMR spectroscopy. After 11 days, this sample was subjected to mass spectrometry analysis. Both NMR spectroscopy and mass spectrometry suggest that the structural integrity is maintained. We note that we observed a small boric acid impurity by $^{11}$B NMR spectroscopy.

**Glutathione:** 16.9 mg of 2i was dissolve in 2.82 mL of D$_2$O. 500 $\mu$L of this solution was added to 100 $\mu$L of a 12 mM glutathione D$_2$O solution. This mixture was vortexed and then transferred to an NMR tube and monitored over 11 days at room temperature by $^1$H, $^{11}$B and $^{19}$F NMR spectroscopy. After 11 days, this sample was subjected to mass spectrometry analysis. Both NMR spectroscopy and mass spectrometry suggest that the structural integrity is maintained. We note that we observed a small boric acid impurity by $^{11}$B NMR spectroscopy as well as some peak broadening in $^{11}$B and $^{19}$F NMR spectra due to the oxidation of 2i from the 2- to the 1- oxidation state over time.
Stability of 2i in Serum

$^{11}$B NMR

![Chemical Structure](image)

- 0.5h
- 1d
- 5d
- 37 °C (+5d)

Graph showing the stability of 2i in serum over time at 37 °C.
Stability of 2i in Serum

$^{19}$F NMR

37 °C (+5d)

5d

1d

0.5h

Bruker
Stability of 2i at pH 5

$^{11}$B NMR
Stability of 2i at pH 5

$^{19}$F NMR
Stability of 2i at pH 7

$^{11}$B NMR
Stability of 2i at pH 7

$^{19}$F NMR
Stability of 2i at pH 9

$^{11}$B NMR

Diagram showing NMR spectra with labels 0.5h, 1d, and 5d.
Stability of 2i at pH 9

$^{19}$F NMR
Stability of 2i in 2-Mercaptoethanol

$^{1}H$ NMR
Stability of 2i in 2-Mercaptoethanol

$^{11}\text{B NMR}$
Stability of 2i in 2-Mercaptoethanol

$^{19}$F NMR
Stability of 2i in 2-Mercaptoethanol - Day 11
Waters Mass Spec
Stability of 2i in Glutathione

$^1$H NMR
Stability of 2i in Glutathione

$^{11}$B NMR
Stability of 2i in Glutathione

$^{19}$F NMR
Stability of 2i in Glutathione - Day 11
Waters Mass Spec
Plot of Conjugation Progress of Boc-cysteine (g) onto Clusters 2/3
Computational work

A. PEGylated OCNs

PEGylated nanoparticles (NPs) \(2i-k\) and \(3i-k\) (see Table 2) were modeled using molecular dynamics (MD) simulations in: \(i\) water with counter ions and \(ii\) a buffer solution of \(\text{HPO}_4^{2-}\) and \(\text{H}_2\text{PO}_4^-\) at a total 0.08 M concentration, where the ratio of the two ions was used matched pH 7.4. The MD simulations were performed with NAMD\(^1\), using the CHARMM force field\(^{11-16}\). \textit{Ab initio} calculations were done with Gaussian09\(^17\) to determine unknown parameters for the dodecaborate cluster center and the non-PEGylated (2 or 3 type ligand) section of the ligand. The boron center was optimized using a HF/6-31g level of theory, with partial charges derived with a ChelpG algorithm\(^18\). Bonds, angles, and dihedrals force constants containing boron atoms were chosen to have relatively large values, approximately equal to those of double bonded or aromatic carbons, so that the boron center would be rigid. The type 2 and 3 ligands had their bond and angle parameters determined at the MP2/6-31g(d)//HF/6-31g level of theory with VMD Force Field Toolkit plugin\(^19\). Unknown dihedral parameters were chosen based on similar atom types in the CHARMM force field\(^{11-16}\). Partial charges were determined through the ChelpG algorithm\(^18\). Amide and PEGylated geometries, parameters, and charges were taken from the CHARMM force field\(^{11-16}\).

Each of the 6 NPs was separately simulated in water and ionic solutions. Each system is first minimized for 10,000 steps. Afterwards it is heated to 310 K, with 1 K increments per 20 steps until the system reaches a temperature of 310 K, when a pre-equilibration is done. Simulations are performed in an NPT ensemble, at 310 K and a pressure of 1 atm, with Langevin dynamics and a damping constant of 0.01 ps\(^{-1}\). Langevin piston is used with a period of 200 fs and decay of 100 fs. Particle Mesh Ewald\(^20\) is used for long range electrostatic interactions with a grid...
spacing of 1.0. Short range interactions are performed with the 12-6 Lennard-Jones potential, using a switching function. Velocity Verlet integration is used with the SHAKE algorithm and a time step of 2 fs. Data and snapshots are recorded every 10 ps or 5,000 steps. Simulation times of 25 ns for the water solution and 30 ns for the salt system were used, respectively. Supplementary Figures 1 and 2 show snapshots of PEGylated NPs in water (21 ns) and in the ionic solution (31 ns), respectively. Notice that as the chain length increases, the chains are fluctuating significantly to the extent that the chain distributions become asymmetric. In the following, we describe some characteristics of these systems.
Supplementary Figure 1. Nanoparticles snapshots in water after 21 ns of simulations. Scale bar is 1 nm. A) 2i B) 3i C) 2j D) 3j E) 2k F) 3k.
Supplementary Figure 2. Nanoparticles snapshots in 0.08 M buffer solution at pH=7.4 (salt) after
31 ns of simulations. Scale bar is 1 nm. A) 2i B) 3i C) 2j D) 3j E) 2k F) 3k.
We use the simulated trajectories of the NPs to calculate the radial distribution functions (RDF), g(r), from Eqn. 1. It gives the relative probability of finding the j\textsuperscript{th} atom at a distance r from the i\textsuperscript{th} atom with respect to the bulk density:

\[ g(r) = \frac{1}{V \rho_N} \sum \delta(r - r_{ij}) . \]  

In Eqn. 1, \( \delta \) is a delta function, \( r_{ij} \) is the distance of i\textsuperscript{th} and j\textsuperscript{th} atoms, and V is a volume, \( \int 4\pi r^2 \, dr \), used in a normalization, and \( \rho_N \) is the number density of the used species (the number of atoms \( N_O \) used in Eqn. 1 divided by the volume of the simulation box). We use Eqn. 1 when we analyze the distribution of C terminal atoms, which are fixed for a given number of ligands (12). When, we consider the distribution of all PEG-chain oxygens (varying number), we remove \( N_O \) (equal the total number of PEG chain oxygens) from \( \rho_N \), by multiplying Eqn.1 by \( N_O \), to get \( g'(r) \), where we account for the growing distributions for longer PEG chains (more oxygens; system volume is fixed).
Supplementary Figure 3. RDFs of 2i–k and 3i–k NPs. $g'(r)$ calculated for A) boron-PEG oxygen atoms in water and B) boron-PEG oxygen atoms in ionic solution. $g(r)$ calculated for C) boron-terminal C atoms in water and D) boron-terminal C atoms in ionic solutions.

In Supplementary Figure 3, we have calculated $g'(r)$ for (A, B) all the oxygens in PEGylated chains and $g(r)$ for (C, D) terminal carbon atoms of the PEGylated chains. All the cases were calculated with respect to all the boron atoms. We can clearly see that as the chain becomes longer, the oxygen (A, B) distributions become wider and their peaks, $r_{\text{max}}$, become slightly shifted to higher values. Steric effects prevent longer PEGylated chains from folding and wrapping close to the B core, therefore, preventing them from significantly affecting $r_{\text{max}}$. The systems present in
water and ionic solutions have almost the same PEG-oxygens distributions. On the contrary, in the terminal carbon (CD) distributions, the peaks maxima, $r_{\text{max}}$, are significantly shifted to higher values with the chain lengths, since the terminal C atoms are further away from the NPs cores, which they cannot reach. In these distributions, we can also see some differences between water and ionic solution cases, revealing that the terminal atoms in long PEGylated chains are slightly more outstretched in ionic solutions.

The $g'(r)$ distributions (Supplementary Figure 3 A, B) are similar for the 2 and 3 types of ligands, except of some deformations present in the 3 types. These deformations slightly shift the 3 type peaks ($r_{\text{max}}$) to smaller values. For all but 2k and 3k terminal carbon RDFs, 3 type ligands have consistently smaller $r_{\text{max}}$ values than their 2 type counterparts (Supplementary Figure 3), even though 3 has an extra aromatic group, slightly increasing the maximum possible ligand length. The extra aromatic group in 3 ligands enhances π-π stacking interactions between the ligands, thus causing the net length to decrease. The split peak in 2i could be related to the fact that the B shell front and back sides can contribute by separate peaks.

The hydrodynamic radii of the studied NPs were estimated from the regions of decaying $g'(r)$ (half value compared to $r_{\text{max}}$) for the cases (A–B) (all oxygens). In water, the hydrodynamic radii of 2i and 3i are 12 Å; 2j and 3j are 15 Å; 2k and 3k are 20 Å. In the ionic solution, 2i, 3i, 2j, and 3j have very similar sizes as in water. At certain times, there are some chains on 2k or 3k that extend outwards, but most of the other chains are folded (Supplementary Figures 1 E, F and 2 E, F). Interestingly, the maxima of distributions for the terminal C atoms in Supplementary Figure 3 C, D match relatively well to the hydrodynamic radii. One can assume that the terminal C atoms are distributed at the surface of the NPs, revealing thus their radii.
To confirm the previous results, next, the radii of gyration, \( \langle r_{\text{gyr}} \rangle \), are also calculated for NPs using Eqn. 2:

\[
r_{\text{gyr}} = \sqrt{\frac{I}{m}} = \sqrt{\frac{\sum_{\text{atoms}} m_i (r_i - r_{\text{com}})^2}{\sum_{\text{atoms}} m_i}}.
\]  

(2)

Here, \( I \) is the moment of inertia of the molecule, \( m \) is the total mass of the molecule formed by individual contributions, \( m_i \), of atoms shifted with respect to a molecular center of mass, \( r_i - r_{\text{com}} \). Time averaged \( \langle r_{\text{gyr}} \rangle \) was calculated by using equation 2 every 10 ps over 26 ns trajectory (water) or 34 ns trajectory (salt solution) and then averaged. Standard deviations and confidence intervals were also computed.

**Supplementary Table 2.** Radii of gyration, \( \langle r_{\text{gyr}} \rangle \), and their confidence intervals for PEGylated species in water and salt solutions.

| Molecule | Solvent     | \( \langle r_{\text{gyr}} \rangle \) (Å) |
|----------|-------------|-----------------------------------------|
| 2i       | water       | 11.5 ± 0.9                              |
| 2j       | water       | 15.0 ± 1.7                              |
| 2k       | water       | 20.7 ± 2.2                              |
| 3i       | water       | 12.1 ± 1.2                              |
| 3j       | water       | 14.7 ± 1.3                              |
| 3k       | water       | 21.1 ± 2.0                              |
| 2i       | ionic solution | 11.7 ± 1.0                       |
| 2j       | ionic solution | 14.7 ± 2.0                       |
| 2k       | ionic solution | 21.0 ± 2.5                       |
| 3i       | ionic solution | 12.2 ± 1.5                       |
| 3j       | ionic solution | 14.8 ± 1.6                       |
| 3k       | ionic solution | 22.1 ± 4.5                       |

Supplementary Table 2 shows the radii of gyration, \( \langle r_{\text{gyr}} \rangle \) and their >99.5 % confidence intervals for PEGylated species in water and salt solutions. As expected, 2i and 3i molecules have the smallest diameters, whereas 2k and 3k have the largest diameters in both environments. 2i and 3i
molecules, with 7 PEGylated oxygens per ligand have diameters of more than 2 nm; 2j and 3j, with 16 PEGylated oxygens per ligand, less than 3 nm; 2k and 3k, with 43 oxygens per ligand, more than 4 nm. NPs with the type 3 ligands tend to have a slightly larger diameter than those with the type 2 ligands. This size increase could be due to the extra aromatic group in type 3 ligands, which is absent in the 2 type ligands. \( \langle r_{\text{gyr}} \rangle \) does not change appreciably between the two environments. However, 2k and 3k ligands are slightly more outstretched in the ionic solutions.

**Supplementary Figure 4.** Distributions of \( r_{\text{gyr}} \) in a) water and b) ionic solutions.

Supplementary Figures 4a and b show the distributions of \( r_{\text{gyr}} \) in water and salt solutions, respectively. The distributions are asymmetrically broadened at higher values for all molecules, especially for long chains. This reflects that a few chains could extend and then fold back. Comparing the radii of gyration, \( \langle r_{\text{gyr}} \rangle \), from Supplementary Table 2 and Supplementary Figure 4 with the above hydrodynamic radii and the most likely positions of terminal C atoms, we can see that all these parameters are in good agreement.

**B. Sugar-coated nanoparticles – protein binding**

MD simulations were also performed to investigate multivalent binding of sugar-coated nanoparticles and proteins. Concanavalin A (Con A) was chosen as the target protein to bind with
multivalent sugar-coated particles (SP) and monovalent β-D glucose (G), respectively. Con A forms quaternary structures, giving at pH 7 a tetramer, having four carbohydrates binding sites (hydrogen bonds)\(^{21}\). In each Con A, up to 15 amino acids can be involved in the carbohydrate binding, while for the monosaccharide binding only five amino acids are involved, including Asn 14, Leu 99, Tyr 100, Asp 208, Arg 228\(^{22}\). In our simulations, the tetramer structure of Con A used was based on X-ray diffraction data (PDB code 1ONA)\(^{22}\). Supplementary Figures 5A and B show the structures of tetramer of Con A with SPs and β-D glucose after 20 ns simulation. The metals manganese (magenta ball) and calcium (cyan ball) were added in Con A according to its metal binding sites\(^{22}\). The monosaccharide binding sites are distinguished from the backbone of Con A by different colors (shown in Supplementary Figure 5). The Con A tetramer has four binding positions. We name the top right position as binding position 1 (B1), bottom right as B2, top left as B3, and bottom left as B4.
Supplementary Figure 5. A) Tetramer of Con A and sugar-coated particles. B) Tetramer of Con A and β-D glucoses. Details of glucose binding shown in both cases.
For the NPs binding, three SPs (SP1, SP2 and SP4) were initially put near the binding sites of chosen monomers. The last SP (SP3) was placed in the cavity between the B1 and B3 binding positions. For the β-D glucose binding, three glucose molecules (G1, G2 and G3) are separately placed at the binding B1, B2 and B3 positions, while the last glucose molecule (G4) was placed between the B3 and B4 binding position. The two systems were immersed in water together with the counter-ions and the simulations were performed with NAMD\textsuperscript{10}.

The bond, angle and dihedral parameters of protein, SPs (nanoparticle 21 in Table 2) and β-D glucose were implemented from the CHARMM\textsuperscript{11–16} force field. The parameters for the boron core and ligands were used the same as in the PEGylated calculations. The nonbonding parameters of Mn\textsuperscript{2+} ions were based on the calculations of Babu et al.\textsuperscript{23}. Nonbonding interactions of SPs were calculated using a cut-off distance of 10 Å, whereas long-range electrostatic interactions were calculated by the PME method\textsuperscript{20} in the presence of periodic boundary conditions. The systems were simulated in the NPT ensemble, using a Langevin dynamics with a damping constant of 0.01 ps\textsuperscript{-1} and a time step of 1 fs.

First, we modeled the coupling between SPs and the Con A tetramer. At each simulation time, we have calculated a distance between each sugar binding site and its nearest ligand in the SP. Supplementary Figure 6 shows a time-dependent distance between the nearest SPs ligand and the Con A tetramer. During the 20 ns simulations, SP1 and SP2 have an average distance of 4 Å, while SP3 and SP4 have an average distance of about 10 Å. Because the initial position of SP3 is far from any binding site, it can’t bind during the short simulations. From Supplementary Figure 5A, we can see that SP3 competes with SP1 for the B1 position, while SP4 shows a different trend. Within 1 ns, SP4 comes near to the Con A tetramer and binds to it. Then, it leaves away and binds
again at 4 ns, when the binding lasts for about 4 ns. After 12 ns, SP4 binds to the Con A tetramer again.

Supplementary Figure 6. Nearest distances between SPs ligands and the Con A tetramer.

Supplementary Figure 6 reveals that when SPs bind to the Con A tetramer their binding distance is about 1.8-2 Å. SPs occasionally gain and preserve for significant time periods these small binding distances. Supplementary Figure 5 A(a-c) show details of SP1, SP2 and SP4 binding to their binding sites. We can see that in all the cases only one of the SPs ligands binds to the nearby binding site, composed of Asn 14, Leu 99, Tyr 100, Asp 208, Arg 228, which is the monosaccharide binding site shown in different color in Supplementary Figure 5 A(a-c). Therefore, there is always one ligand of SPs which performs like a monosaccharide when binding to the Con A tetramer. Because the SPs have several ligands, when one ligand leaves, another
nearby ligand comes and binds, which increases the binding probability of SPs. In this way, SPs act like multivalent binders.

Supplementary Figure 7. Nearest distances between β-D glucose molecules and the Con A tetramer.

In order to compare the binding ability of SPs and β-D glucose systems, we simulated binding of β-D glucose and the Con A tetramer. Supplementary Figure 7 shows the nearest distance between β-D glucose and Con A as a function of time. Supplementary Figure 7 shows that G1 only binds to Con A at the first 1 ns and then leaves. G2 only binds at the very beginning and it doesn’t bind later; G3 binds to Con A for about 4 ns at the beginning and after that it leaves away; G4 shows weak binding during the first 4 ns. The average distance between all the β-D glucose molecules and the Con A tetramer is more than 20 Å, except G3 whose average distance is about 12 Å. Supplementary Figure 5B(a-c) shows details of β-D glucose and the Con A tetramer binding.
When β-D glucose binds to Con A, it binds to the typical monosaccharide binding sites. Because β-D glucose is monovalent, when one β-D glucose leaves, another β-D glucose from the surrounding solution might come nearby and bind. Overall, monovalent β-D glucose molecules show shorter binding times and longer binding distances than SPs.
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