

Supporting Information

Dendritic Closures: Novel Spherical Hybrid Dendrimers

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General methods

Bulk solvents were purchased from VWR International (West Chester, PA) and were used as received. Ethanol was purchased from Decon Labs, Inc. Ethyl 4-bromobutyrate was purchased from Alfa Aesar. All other reagents were purchased from Acros. All chemicals were used without further purification. Water was obtained from a Barnstead NANOpure Water Purification System operating at $18.2 \text{ M}\Omega \times \text{cm}$. Dodecahydroxy *closo*-dodecaborane **1** was synthesized according to a previously reported protocol.^{1,2}

NMR spectra were recorded on Bruker AVANCE^{III}-400 and AVANCE-500 instruments. Chemical shifts (δ , ppm) for ¹H and ¹³C were referenced to residual solvent peaks. Boron chemical shifts were externally referenced to BF₃·Et₂O and the width of boron NMR signal was calculated at half height of a corresponding peak. UV-Vis absorption spectra were recorded on Varian Cary 50 spectrophotometer. Mass spectra were obtained using Waters/Micromass Q-TOF *Ultima* API and PerSeptive-ABI Mariner (ESI-TOF) instruments. High resolution mass spectra (HRMS) were acquired on Bruker APEX-Ultra 7T FT-ICR instrument. Data reported as follows: (m/z: calculated; m/z: found). The isotopic distribution of each dodecaborane containing ion matched that expected for normal abundance boron. Particle size was determined via dynamic light scattering on Microtrac Zetatrak instrument.

Size exclusion chromatography was performed using Sephadex LH-20 resin on Agilent EZChrom SI System - EZPump Series II/Series III equipped with Model 500 UV-Vis Detector, 50x600 mm Michel-Miller glass column and Teledyne Isco Foxy 200 automatic fraction collector.

Analytical HPLC traces were acquired on Beckman Coulter System Gold 125NM Solvent Module and 168 PDA Detector; column Jupiter 4 μm Proteo 90Å (250x4.60 mm Phenomenex C12); flow 1 mL/min; Gradient: B 0% to 100% over 100 min; A: water + 0.1% TFA, B: acetonitrile + 0.1% TFA.

Preparative HPLC purification was carried out on Beckman Coulter System Gold 126 Solvent Module and 168 PDA Detector; column DYNAMAX-150A (400x20 mm Rainin C18); flow 10 mL/min; Gradient: B 0% 1 min, then B 0% to 50% over 50 min; A: water + 0.1% TFA, B: acetonitrile + 0.1% TFA.

Cyclic voltammetry was conducted using Princeton Applied Research *PARSTAT 2273 Advanced Electrochemical System* interfaced with a computer running PowerSuite 2.60 software. Experiments utilized a PAR microcell equipped with a Pt quasi-reference electrode calibrated vs Fc/Fc⁺ couple. Experiments were conducted in 0.10 M solution of tetrabutylammonium hexafluorophosphate prepared in freshly distilled acetonitrile de-aerated with argon. Neutral ether closomers were used in concentrations of 1 mM. The electrochemical experiments were carried out using scan rates of 50, 100, and 200 mVs⁻¹. Half-wave potentials ($E_{1/2}$) for each electrochemical reaction were calculated from the equation $E_{1/2} = (E_{pc} + E_{pa})/2$ using the cathodic and anodic peak current potentials E_{pc} and E_{pa} , respectively. Each measurement given herein is an average of three trials. Each cyclic voltammetry experiment was conducted with and without the presence of ferrocene as an internal reference.

Synthesis of dendritic closomer 2. (i) Alkylation of $B_{12}(OH)_{12} \cdot 2TBA$ (1**) with ethyl 4-bromobutyrate.** A two-necked round-bottom flask was charged with **1** (5.09 g, 6.20 mmol), ethyl 4-bromobutyrate (54 mL, 0.38 mol), diisopropylethylamine (21 mL, 0.12 mol) and acetonitrile (200 mL). The vigorously stirred mixture was heated to reflux under argon. In 5 days, another portion of diisopropylethylamine (11 mL, 0.06 mol) was added to the reaction mixture. In another 5 days an additional portion of diisopropylethylamine (11 mL, 0.06 mol) was added to the reaction mixture. In another 5 days an additional portion of diisopropylethylamine (11 mL, 0.06 mol) was added to the reaction mixture. After 5 days of last addition of diisopropylethylamine the reaction mixture was concentrated in *vacuo* to a constant volume. The viscous residue was dissolved in ethyl acetate (500 mL) and the solution was filtered. The filtrate was concentrated in *vacuo* to a constant volume and the remaining residue was washed with hexane (3x300 mL). The residue was dissolved in methanol and purified on Sephadex LH-20 (50x600) using methanol as eluent at the rate of 10 mL/min, 254 nm. The product was eluted between 50 and 59 min; combined fractions were concentrated in *vacuo* to dryness. Yield 9.5 g (79%). ^{11}B NMR (MeCN, 128 MHz) δ -16.8 (signal width 239.5 Hz); **(ii) Oxidation of the alkylation product into hypercloso form 2.** The alkylation product was dissolved in a minimal amount of dichloromethane and passed through SiO_2 column, eluent dichloromethane-ethanol 9:1 giving the corresponding oxidized bright orange colored hypercloso compound. The eluted product fractions were concentrated in *vacuo* to dryness and the target 12-fold butyrate was additionally passed through a SiO_2 column, slurry packed with a 1:1 mixture of hexane-ethyl ether, eluent: first 200 mL 1:1 mixture of hexane-ethyl ether, then additionally 200 mL of ethyl ether to give 2.40 g of pure product; combined yield for two stages was 23%. ^{11}B NMR (CDCl_3 , 160 MHz) δ 41.6 (signal width 155.8 Hz). ^1H NMR (CDCl_3 , 500 MHz) δ 4.06 (24H, q, OCH_2CH_3), 3.96 (24H, t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 2.28 (24H, t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 1.81 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 1.17 (24H, t, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.3, 69.7, 60.3, 30.9, 27.4, 14.2. HRMS-ESI(-) M^+ calc 1704.9615, M^+ found 1705.0369.

Synthesis of dendritic closomer 3. To a stirred solution of ethylenediamine dihydrochloride (0.47 g, 3.52 mmol) in ethylenediamine (50 mL), a solution of **2** (1.00 g, 0.59 mmol) in ethanol (5 mL) was slowly added dropwise at r.t. under argon over a period of 10 min. The reaction was stirred at r.t. for 3 days (monitoring by MS-ESI). The solution was concentrated in *vacuo* to dryness and the residue was purified on Sephadex LH-20 (50x600), methanol 10 mL/min, 254 nm. The product was eluted between 45 and 59 min; combined fractions were concentrated in *vacuo* to dryness. Yield 1.00 g (90%). ^{11}B NMR (D_2O , 160 MHz) δ -16.9 (signal width 166.0 Hz); ^1H NMR (D_2O , 500 MHz) δ 3.91 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 3.37 (22H, m, $\text{NCH}_2\text{CH}_2\text{NH}$), 3.20 (2H, t, $\text{NCH}_2\text{CH}_2\text{N}$), 3.09 (2H, t, $\text{NCH}_2\text{CH}_2\text{N}$), 2.96 (22H, m, $\text{NCH}_2\text{CH}_2\text{N}$), 2.27 (24H, t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 1.77 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$); ^{13}C NMR (D_2O , 125 MHz) δ 177.3, 65.7, 40.5, 40.0, 39.3, 38.7, 32.8, 28.2; HRMS-ESI(+) $[\text{M}+3\text{H}]^+$ calc 1876.3076, found 1876.37069, $[\text{M}+4\text{H}]^{2+}$ calc 938.6577, found 938.6401.

Synthesis of dendritic closomer 4. To a stirred solution of **3** (3.50 g, 1.87 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.50 g, 3.74 mmol) in ethanol (40 mL) ethyl acrylate (40 mL) and diisopropylethylamine (7.8 mL, 45 mmol) were sequentially added. The reaction was stirred at r.t. for 24 h. Then more methyl acrylate (20 mL) was added. The reaction mixture was stirred for 18 days at r.t. while monitoring its progress by MS-ESI. The mixture was concentrated in *vacuo* to dryness and the residue was purified on Sephadex LH-20 (50x600), methanol 10 mL/min, 254 nm. The product was eluted between 34 and 45 min; combined fractions were concentrated in *vacuo* to dryness. Yield 4.33 g (42%). ^{11}B NMR (MeCN, 160 MHz) δ -16.5 (signal width 272.9 Hz); HRMS-ESI(+) $[\text{M}+3\text{H}]^{2+}$ calc 2138.7898, found 2138.7885, $[\text{M}+4\text{H}]^{3+}$ calc 1426.1958, found 1426.1990.

Synthesis of dendritic closomer 5. To a stirred solution of ethylenediamine dihydrochloride (0.93 g, 7.00 mmol) in ethylenediamine (75 mL) a solution of **4** (2.48 g, 0.58 mmol) in ethanol (6 mL) was added dropwise at r.t. over a period of 10 min under argon. Then the reaction mixture was stirred at r.t.

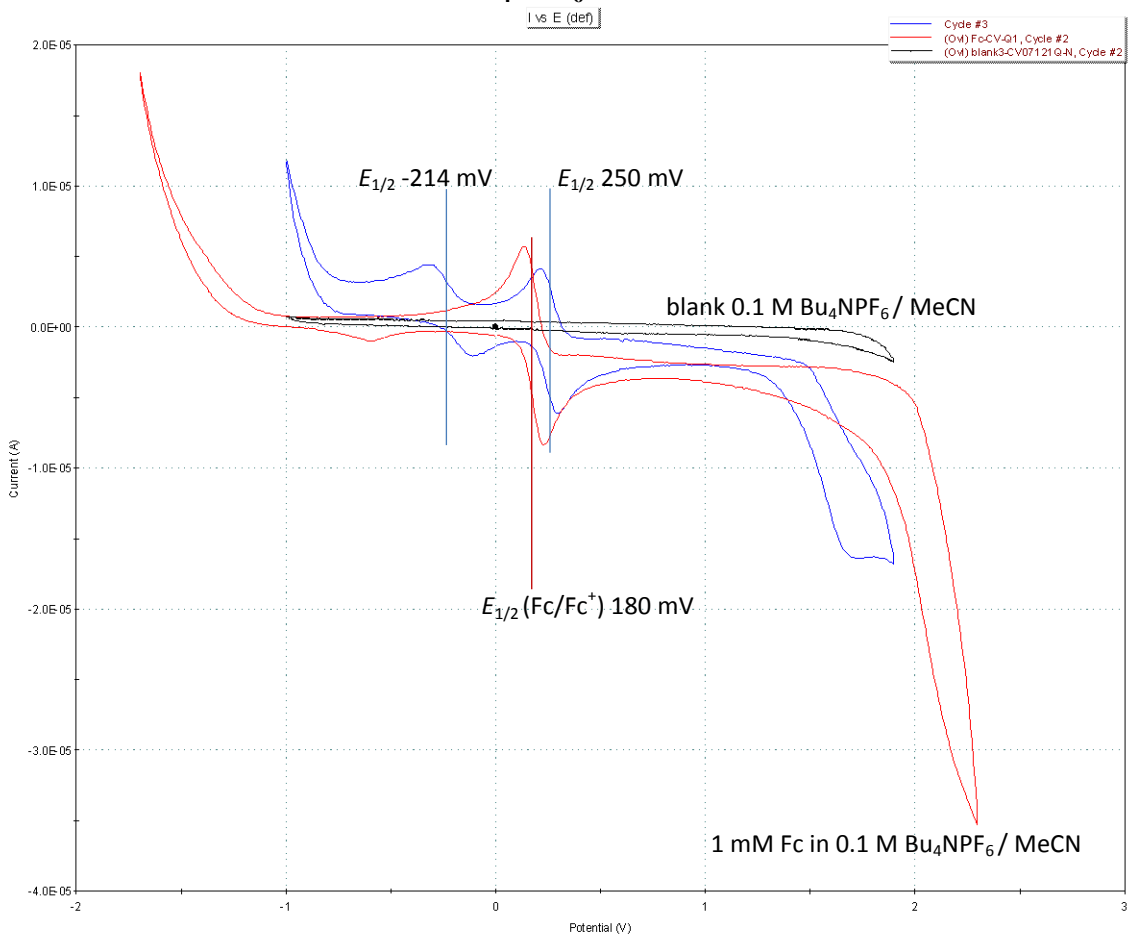
for 3 days (monitoring by MS-ESI). Upon completion the reaction mixture was concentrated in *vacuo* to dryness and separated on Sephadex LH-20 (50x600), methanol 10 mL/min, 254 nm. Product was eluted between 41 and 55 min. Combined fractions were concentrated in *vacuo* to dryness. Yield 1.55 g (58%). ^{11}B NMR (D_2O , 128 MHz) δ -17.2 (signal width 161.5 Hz); ^1H NMR (D_2O , 400 MHz) δ 3.87 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 3.24 (72H, m), 2.77 (96H, m), 2.55 (24H, m), 2.37 (48H, t) 2.19 (24H, t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 1.72 (24H, m, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$); ^{13}C NMR (D_2O , 125 MHz) δ 176.4, 175.1, 65.5, 51.4, 49.1, 40.2, 39.6, 36.6, 32.9, 32.7, 28.5; HRMS-ESI(-) M^{2-} calc 2305.6009, M^{2-} found 2305.5571, HRMS-ESI(+) $[\text{M}+5\text{H}]^{3+}$ calc 1538.7470, found 1538.9352, $[\text{M}+6\text{H}]^{4+}$ calc 1154.3122, found 1154.5360, $[\text{M}+7\text{H}]^{5+}$ calc 923.6513, found 923.9562.

Synthesis of dendritic closomer 6. To a stirred solution of **5** (0.70 g, 0.15 mmol) and 4-(N,N-dimethylamino)pyridine (0.02 g, 0.16 mmol) in ethanol (10 mL) ethyl acrylate (13 mL) and diisopropylethylamine (1.3 mL, 7.52 mmol) were sequentially added. The reaction was stirred at r.t. for 24 h. Then an additional 13 mL of methyl acrylate was added. The reaction was stirred at r.t. for 18 days while monitoring its progress by MS-ESI. The mixture was concentrated in *vacuo* to dryness and the residue was purified on Sephadex LH-20 (50x600), methanol 10 mL/min, 254 nm. The product was eluted between 34 and 44 min; combined fractions were concentrated in *vacuo* to dryness. Yield 1.13 g (80%). ^{11}B NMR (MeCN, 128 MHz) δ -17.2 (signal width 262.9 Hz); HRMS-ESI(-) M^{2-} calc 4708.3642, M^{2-} found 4708.3613. Due to the paramagnetic nature (ion-radical) of compound **6** its ^1H and ^{13}C NMR spectra are very broad and unresolved.

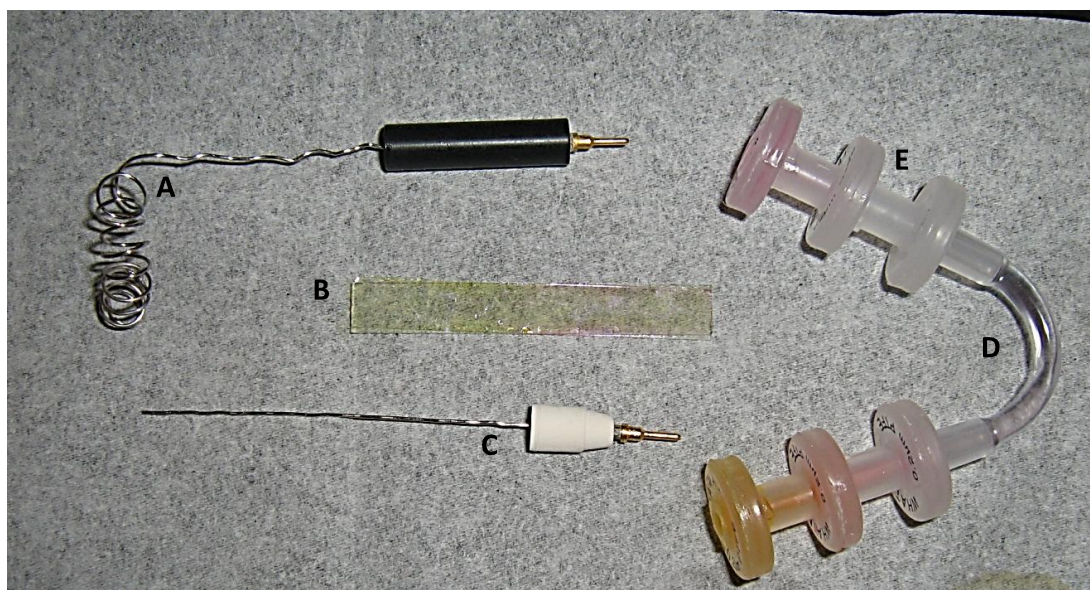
Synthesis of dendritic closomer 7. To a vigorously stirred solution of ethylenediamine dihydrochloride (0.20 g, 1.50 mmol) in ethylenediamine (30 mL), a solution of **6** (0.55 g, 0.06 mmol) in ethanol (3 mL) was slowly added at r.t. over interval of 10 min under argon. The reaction was stirred at r.t. for 3 days (monitoring by MS-ESI). Upon completion the reaction mixture was concentrated in *vacuo* to dryness and separated on Sephadex LH-20 (50x600), methanol 10 mL/min, 254 nm. Product was eluted between 34 and 40 min. Combined fractions were concentrated in *vacuo* to dryness. Yield 0.28 g (46%). ^{11}B NMR (D_2O , 160 MHz) δ -17.2 (signal width 136.0 Hz); ^1H NMR (D_2O , 500 MHz) δ 3.93 (24H, br, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 3.25 (168H, m), 2.79 (144H, t), 2.73 (96H, m), 2.60 (72H, m) 2.41 (144H, t), 2.24 (24H, br, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$), 1.72 (24H, br, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CO}_2$); ^{13}C NMR (D_2O , 125 MHz) δ 176.4, 175.1, 174.4, 65.6, 51.5, 51.3, 49.1, 40.6, 39.7, 36.7, 33.0, 32.8, 28.5. See p. S24 for the mass spectrum deconvolution using the massXpert 2 software.³

Encapsulation of Doxorubicin (DOX) in dendritic closomer 7. A solution of **7** (100 μL , 2.3 mM in 10 mM ammonium acetate) was mixed with a DOX solution (12 mM in 1:1 MeOH/DMF) in 1:3 and 1:6 molar ratios, 58 μL and 116 μL , respectively. The mixtures were dissolved in methanol (2 mL) and stirred at r.t. for 24 h, then 0.5 mL of water (18.2 $\text{M}\Omega \times \text{cm}$) was added to each vial. The mixtures were stirred at r.t. for 48 h and then concentrated in *vacuo* to dryness. The residues were resuspended in 1 mL of 10 mM ammonium acetate (pH 6.5) and these solutions were passed through PD-10 desalting columns (Sephadex G-25M) eluting with water (18.2 $\text{M}\Omega \times \text{cm}$). First 4 ml of eluent (excluded volume) were collected and concentrated in *vacuo* to dryness. The concentration of DOX was determined via measuring the UV/Vis absorbance at 481 nm, ϵ 10410 $\text{M}^{-1}\text{cm}^{-1}$, the dendrimer concentration was determined by ^1H NMR.

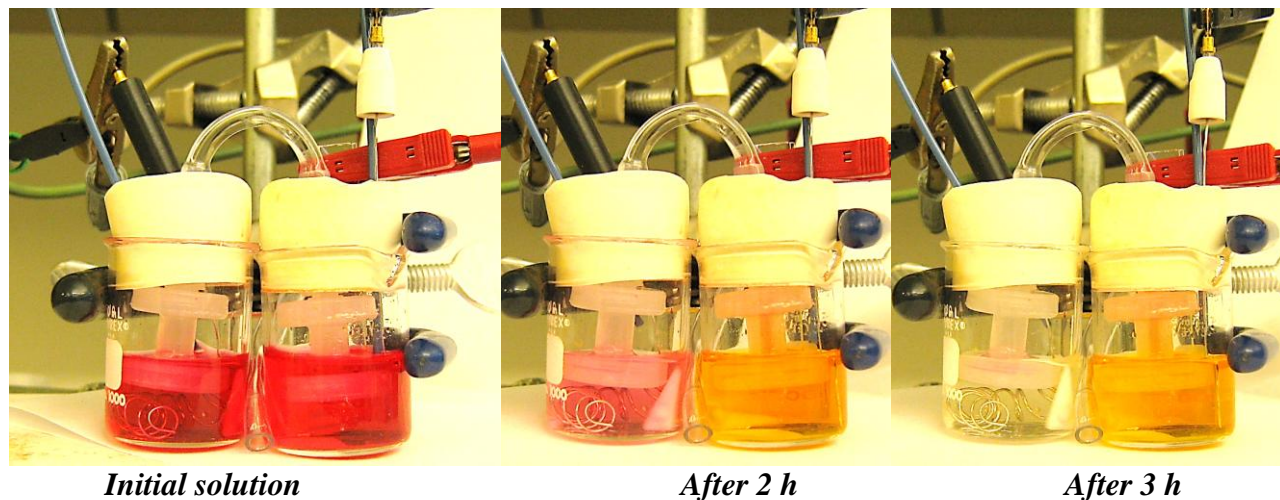
CV of 1 mM solution of 2 in 0.1 M Bu₄NPF₆ / MeCN



Electrochemistry of a mixture of $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{2-}$ and $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{1-}$. Two-compartment electrochemical cell: (A) Pt working electrode, (B) double sided ITO covered glass (35 Ω) counter electrode, (C) Pt quasi-reference electrode, (D) salt bridge, membranes connected with a Tygon tube and filled with 0.1 M Bu₄NPF₆ in acetonitrile, (E) membrane, 3 joined Whatman 13 mm syringe filters (0.2 μ m pore size PTFE) per compartment.

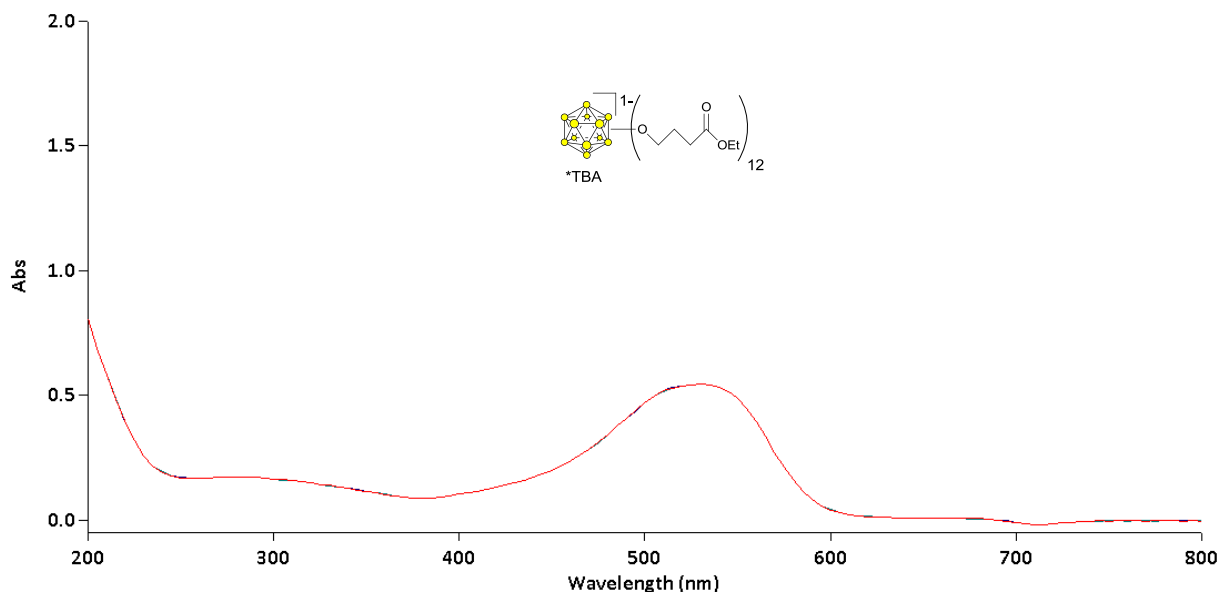


An intensely red mixture of $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{2-}$ and $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{1-}$ (0.17 g, ~ 0.08 mmol) was dissolved in de-aerated, dry acetonitrile (1 mL) resulting in ~ 80 mM stock solution. The 63 μ L aliquot was mixed with 10 mL of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile resulting in ~ 0.5 mM solution. Under argon atmosphere each compartment of the electrochemical cell was charged with 4 mL of the 0.5 mM solution of the mixture in the electrolyte. The working electrode potential was set to -1.3 V, initial current 20 μ A. The electrolysis was conducted over period of 3 h, the final current was stabilized at 10 μ A. Completion of the reaction was monitored visually and by UV-Vis spectroscopy of the content of each compartment.

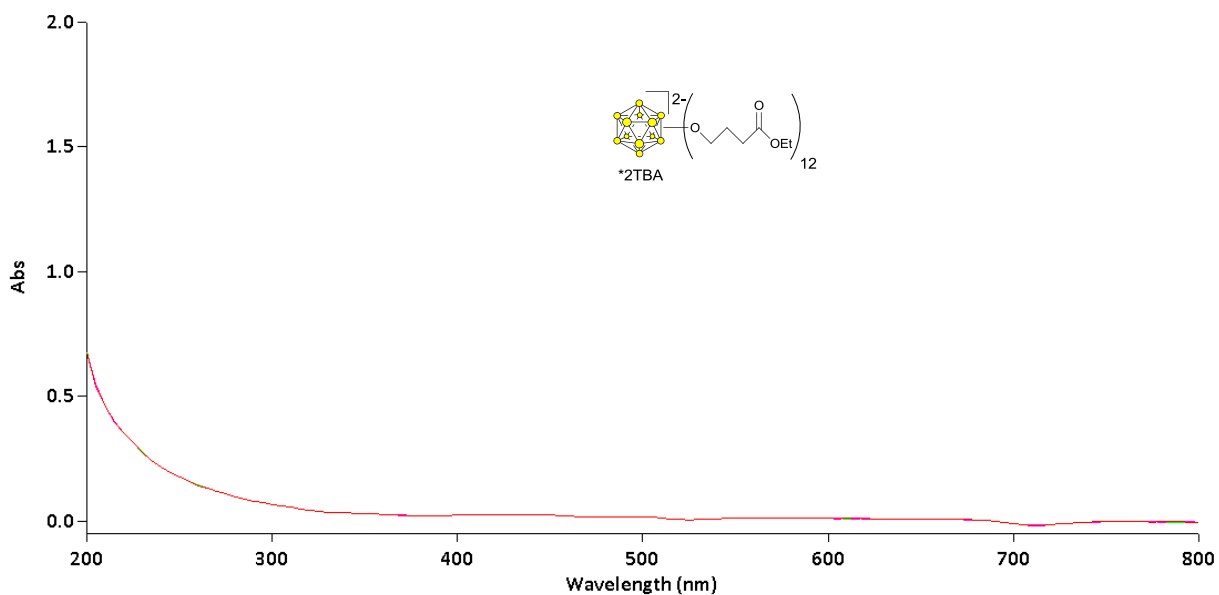


According to the UV-Vis control, after 3 h the content of both cathodic and anodic compartments was completely converted into the respective oxidation states. When stored in tightly sealed containers, the color of these solutions remained effectively unchanged for a period more than a week (monitoring timespan).

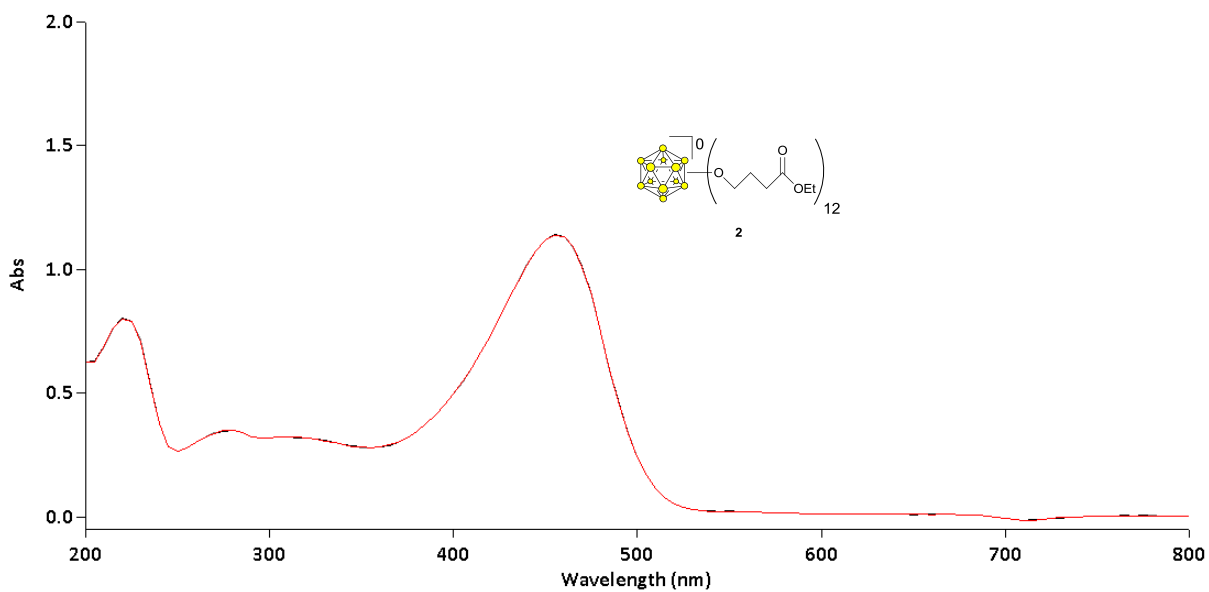
UV-Vis spectra of 0.5 mM solutions for various oxidation states of $B_{12}[O(CH_2)_3CO_2Et]_{12}$



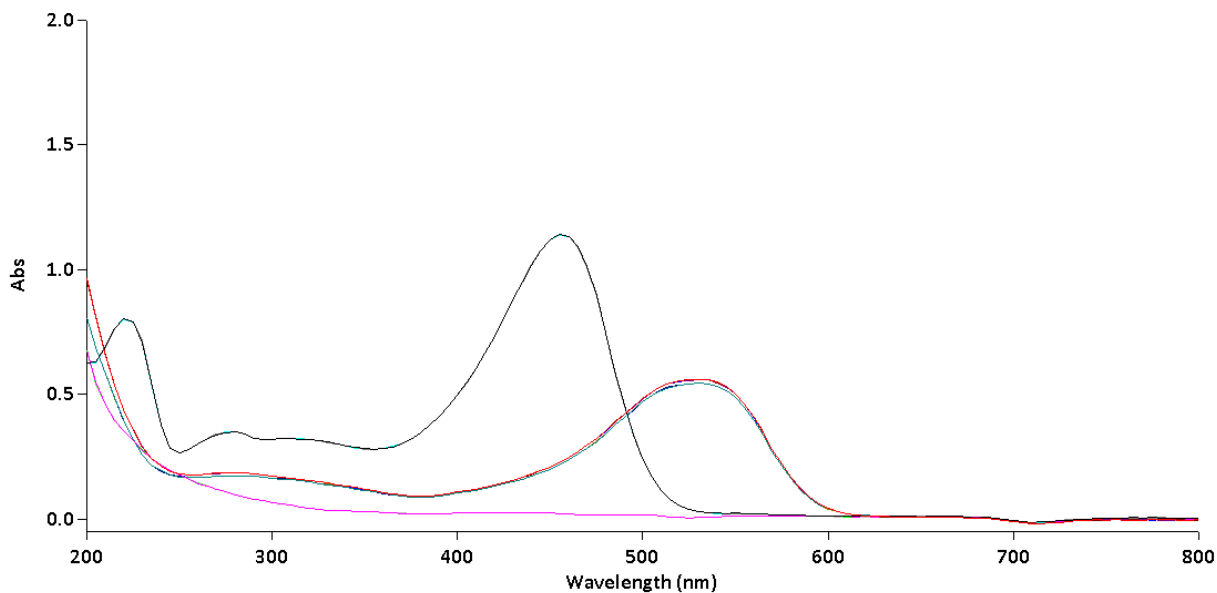
- a) Mixture of $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{2-}$ and $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{1-}$ in acetonitrile, identical to UV-Vis spectrum of the solution of the same concentration in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile



b) Content of the cathode compartment, in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile

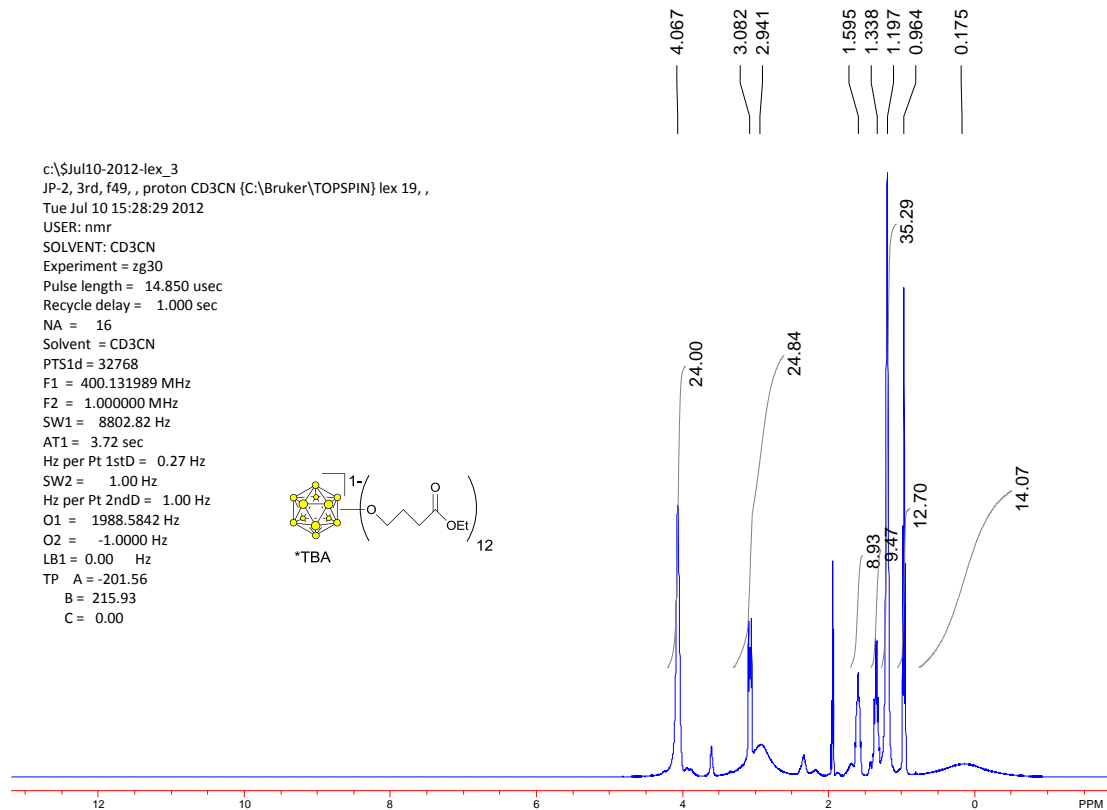


c) Content of the anode compartment, in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile; identical to UV-Vis spectra of the pure compound **2** in acetonitrile

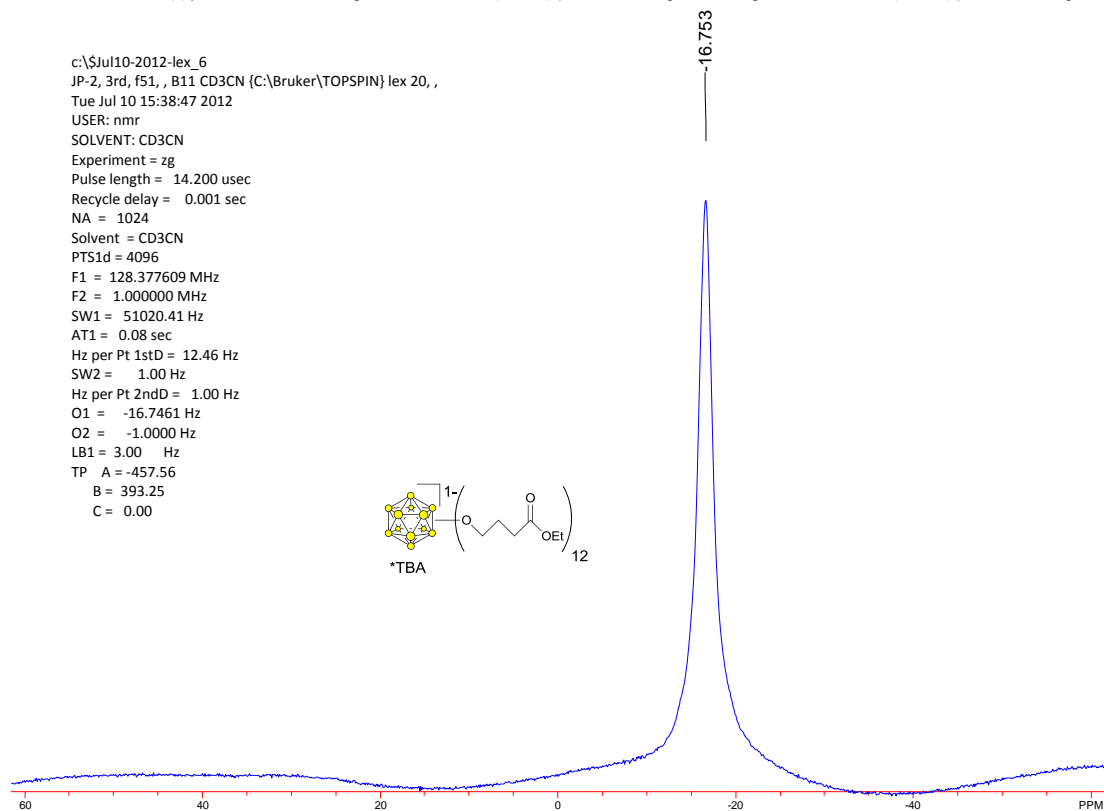


d) All UV-Vis spectra superimposed

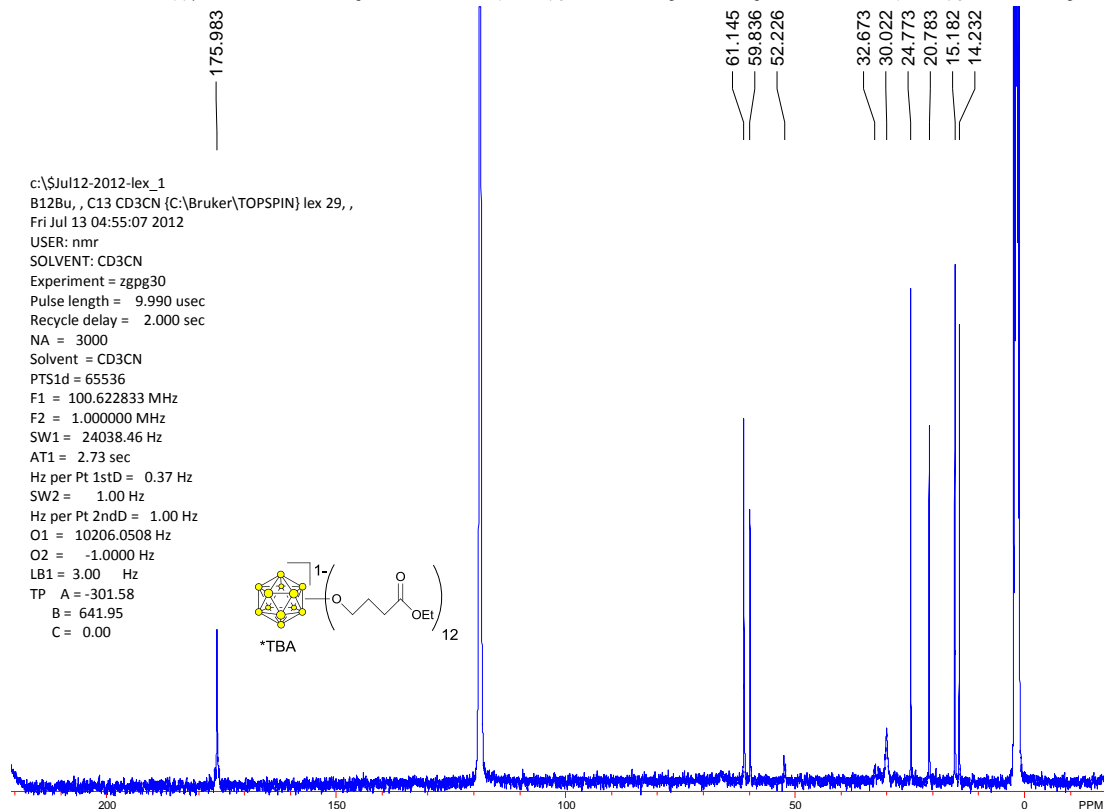
^1H NMR of 2(i), a mixture of $\{\text{closo-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{2-}$ and $\{\text{closo-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{1-}$



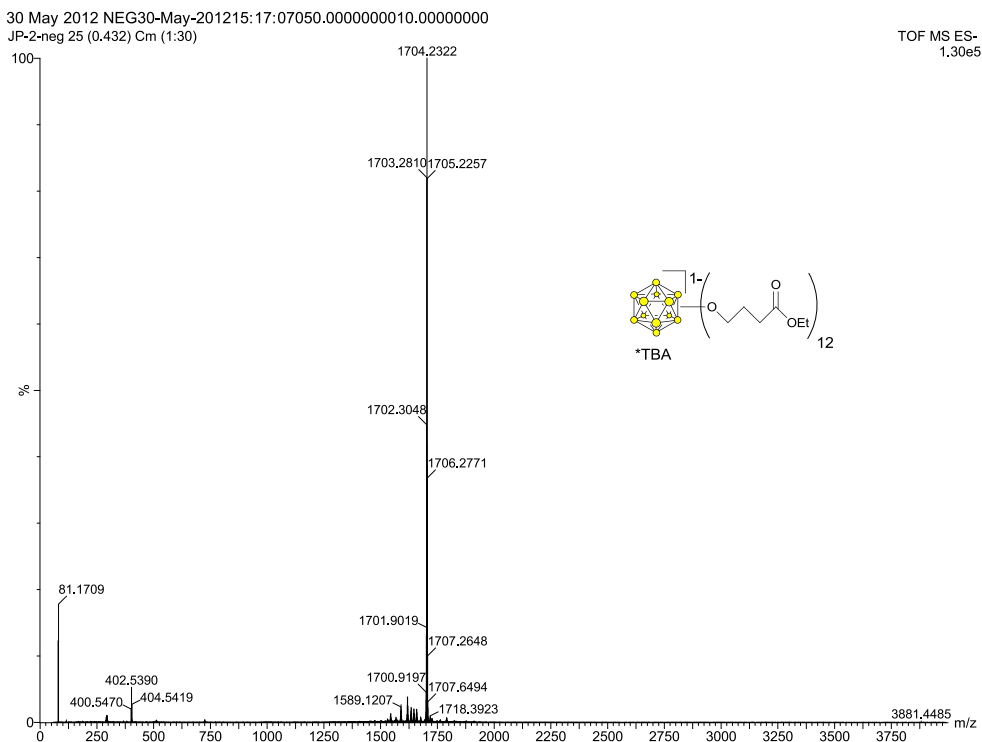
^{11}B NMR of 2(i), a mixture of $\{\textit{closo}\text{-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{2-}$ and $\{\textit{closo}\text{-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{1-}$



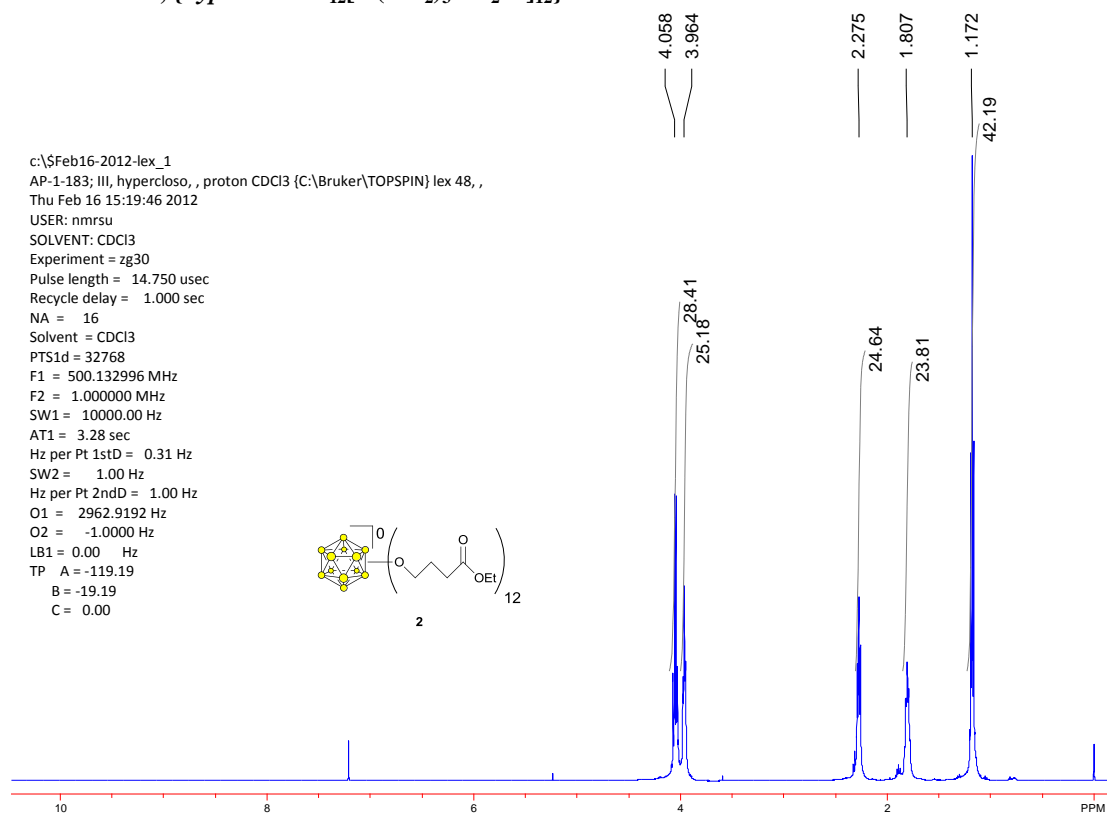
^{13}C NMR of 2(i), a mixture of $\{\textit{closo}\text{-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{2-}$ and $\{\textit{closo}\text{-B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}\}^{1-}$



MS of 2(i), a mixture of $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{2-}$ and $\{closo-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^{1-}$

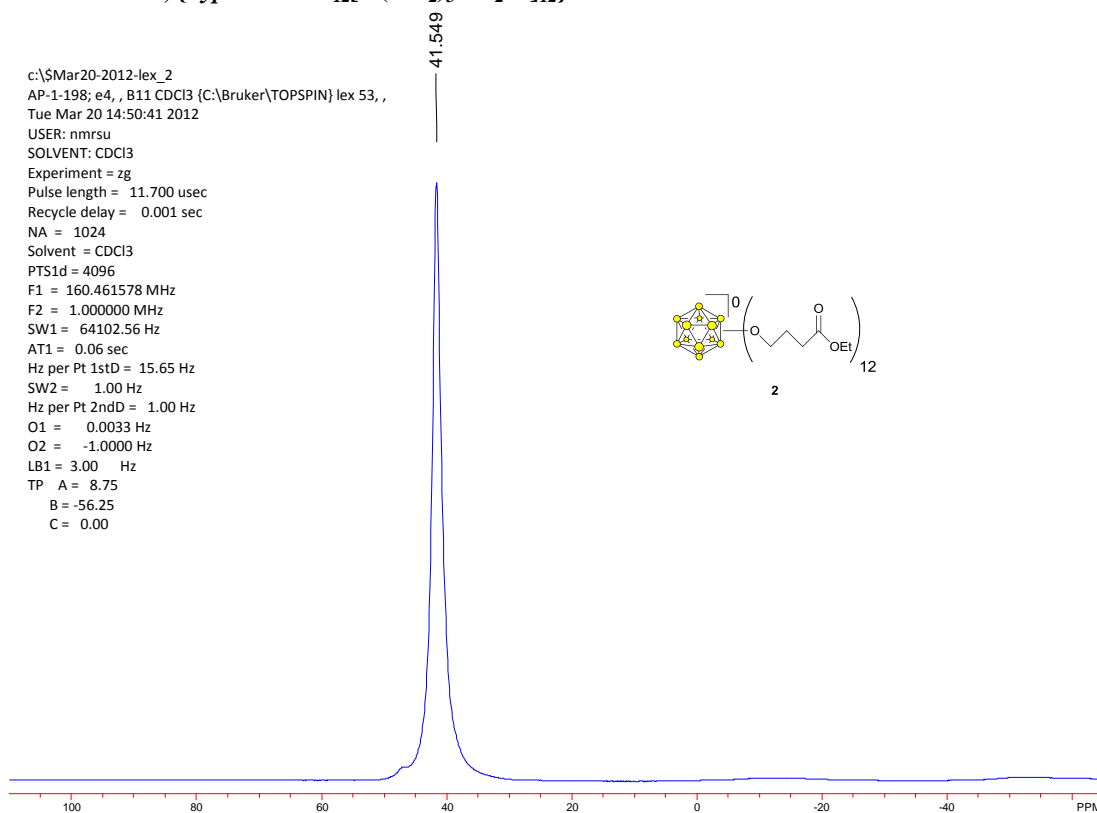
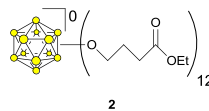


1H NMR of 2, $\{hypercloso-B_{12}[O(CH_2)_3CO_2Et]_{12}\}^0$



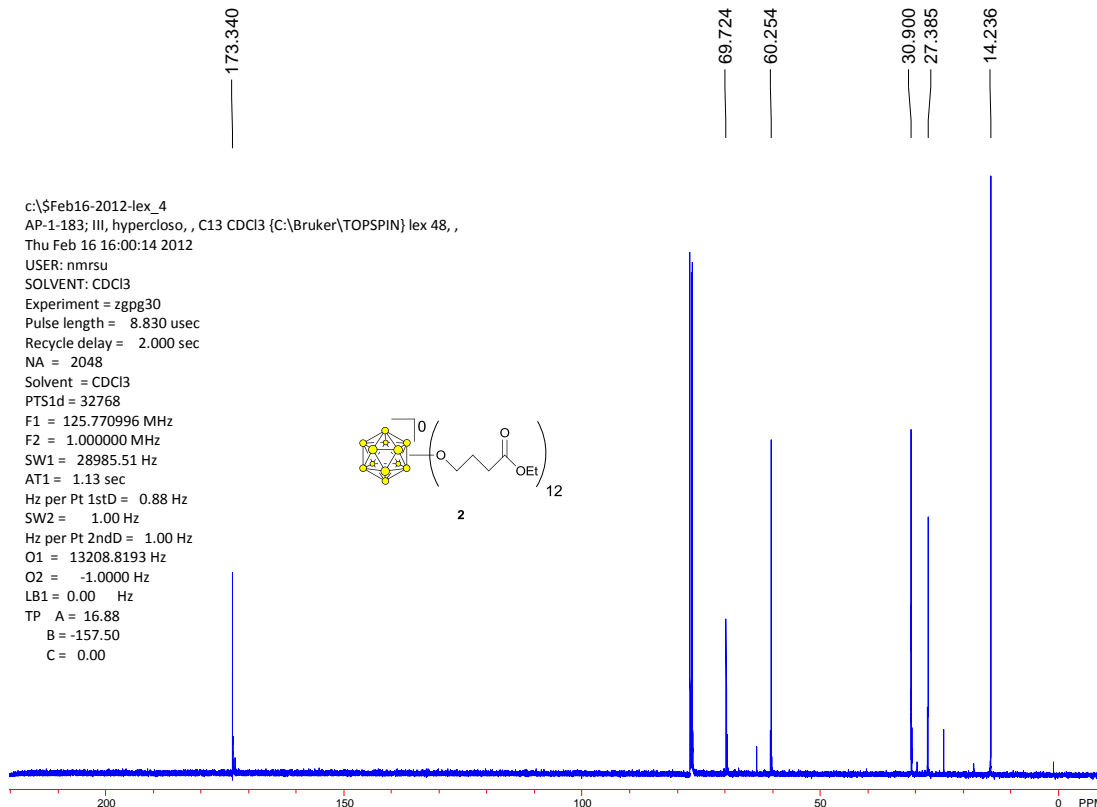
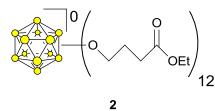
^{11}B NMR of 2, {hypercloso- $\text{B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}$ } 0

c:\\$Mar20-2012-lex_2
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Recycle delay = 0.001 sec
NA = 1024
Solvent = CDCl₃
PTS1d = 4096
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F2 = 1.000000 MHz
SW1 = 64102.56 Hz
AT1 = 0.06 sec
Hz per Pt 1stD = 15.65 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 0.0033 Hz
O2 = -1.0000 Hz
LB1 = 3.00 Hz
TP A = 8.75
B = -56.25
C = 0.00



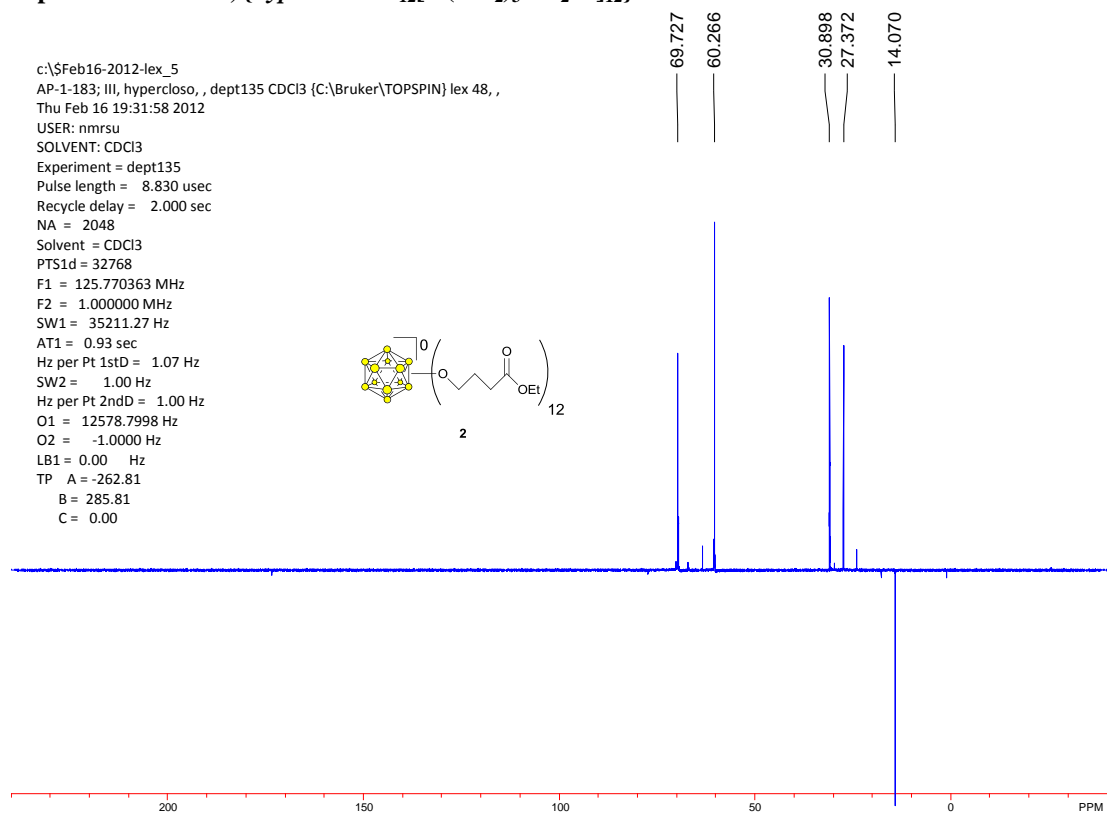
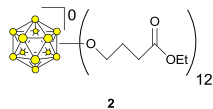
^{13}C NMR of 2, {hypercloso- $\text{B}_{12}[\text{O}(\text{CH}_2)_3\text{CO}_2\text{Et}]_{12}$ } 0

c:\\$Feb16-2012-lex_4
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Solvent = CDCl₃
PTS1d = 32768
F1 = 125.770996 MHz
F2 = 1.000000 MHz
SW1 = 28985.51 Hz
AT1 = 1.13 sec
Hz per Pt 1stD = 0.88 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 13208.8193 Hz
O2 = -1.0000 Hz
LB1 = 0.00 Hz
TP A = 16.88
B = -157.50
C = 0.00

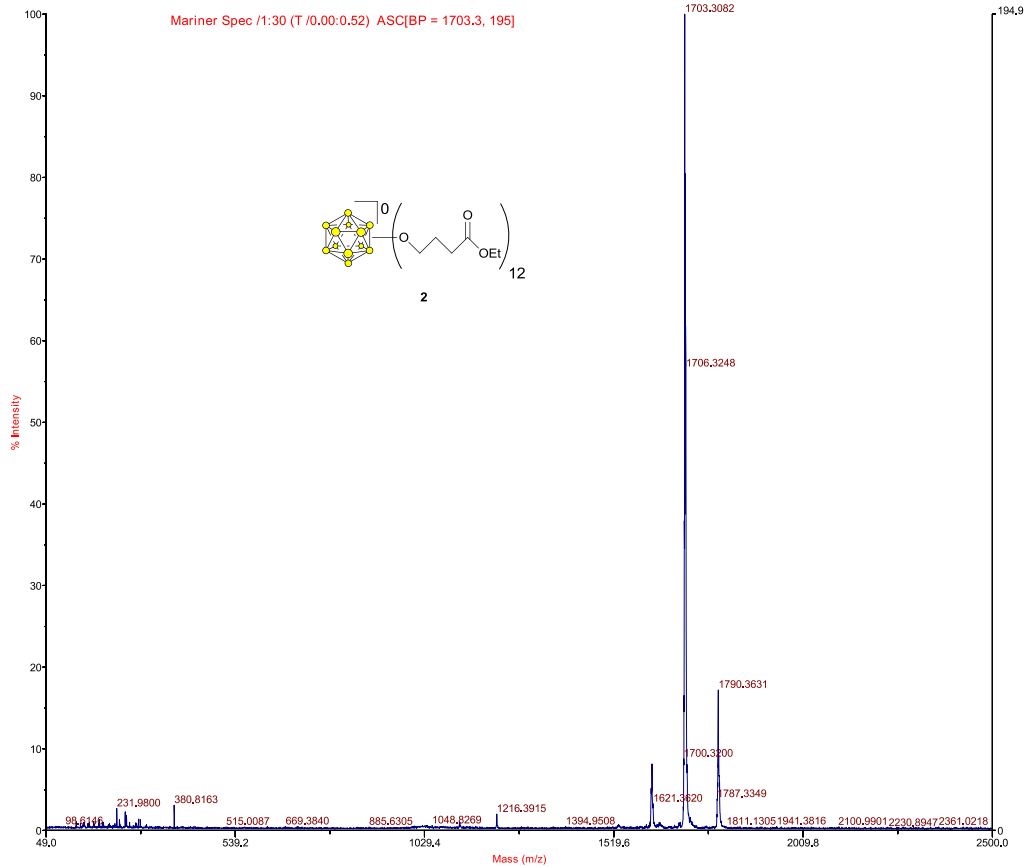


dept-135 NMR of 2, {hypercloso-B₁₂[O(CH₂)₃CO₂Et]₁₂}⁰

c:\Feb16-2012-lex_5
AP-1-183; III, hypercloso, , dept135 CDCl₃ (C:\Bruker\TOPSPIN) lex 48, ,
Thu Feb 16 19:31:58 2012
USER: nmrsu
SOLVENT: CDCl₃
Experiment = dept135
Pulse length = 8.830 usec
Recycle delay = 2.000 sec
NA = 2048
Solvent = CDCl₃
PTS1d = 32768
F1 = 125.770363 MHz
F2 = 1.000000 MHz
SW1 = 35211.27 Hz
AT1 = 0.93 sec
Hz per Pt 1stD = 1.07 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 12578.7998 Hz
O2 = -1.0000 Hz
LB1 = 0.00 Hz
TP A = -262.81
B = 285.81
C = 0.00

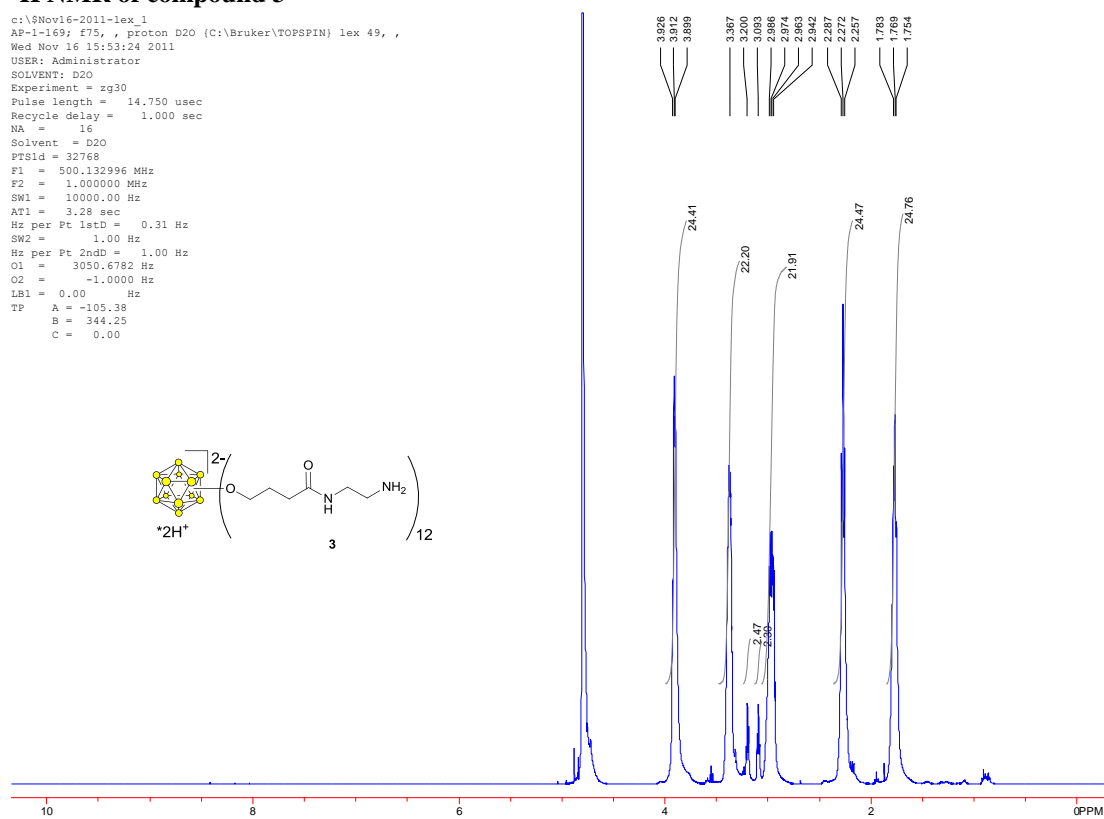
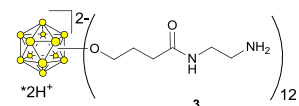


MS of 2, {hypercloso-B₁₂[O(CH₂)₃CO₂Et]₁₂}⁰



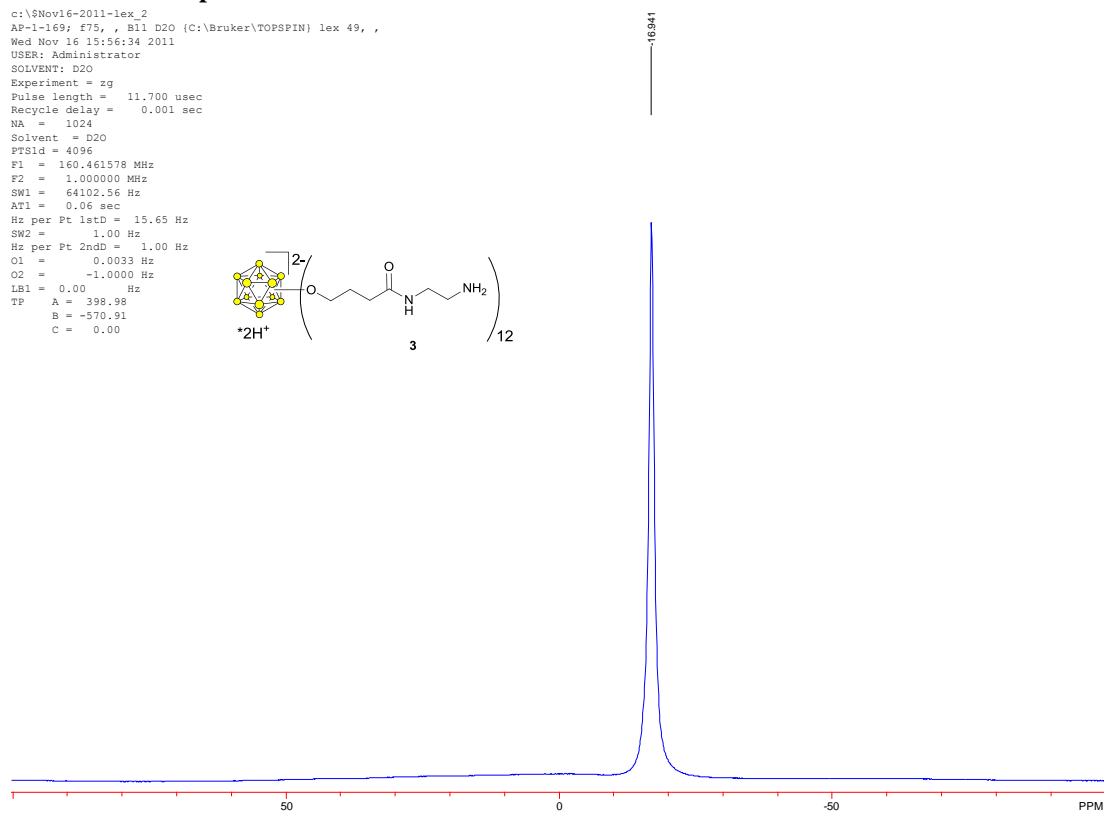
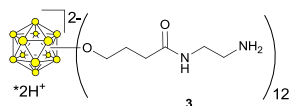
¹H NMR of compound 3

c:\Nov16-2011-lex_1
 AP-1-169; f75, , proton D2O (C:\Bruker\TOPSPIN) lex 49, ,
 Wed Nov 16 15:53:24 2011
 USER: Administrator
 SOLVENT: D2O
 Experiment = zg30
 Pulse length = 14.750 usec
 Recycle delay = 1.000 sec
 NA = 16
 Solvent = D2O
 P1 = 32768
 F1 = 500.132996 MHz
 F2 = 1.000000 MHz
 SW1 = 10000.00 Hz
 AT1 = 3.28 sec
 Hz per Pt 1stD = 0.31 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = 3050.6782 Hz
 O2 = -1.0000 Hz
 LB1 = 0.00 Hz
 TP A = -105.38
 B = 344.25
 C = 0.00

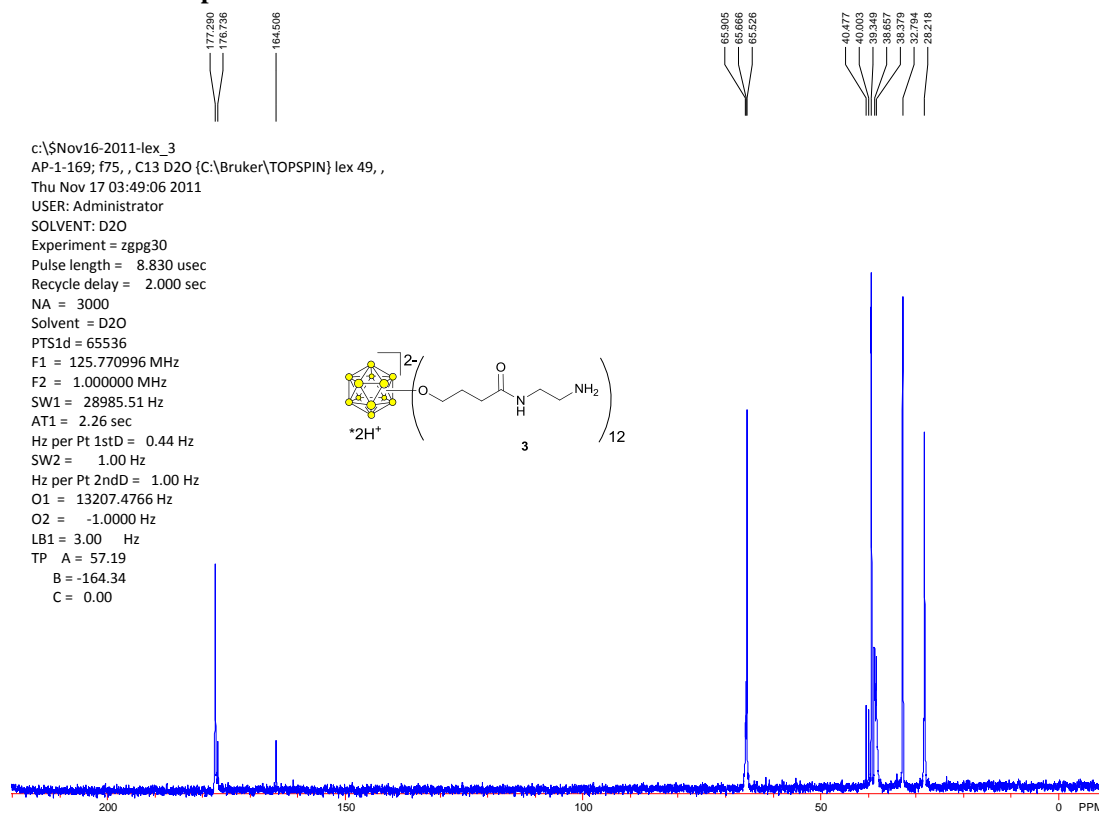


¹¹B NMR of compound 3

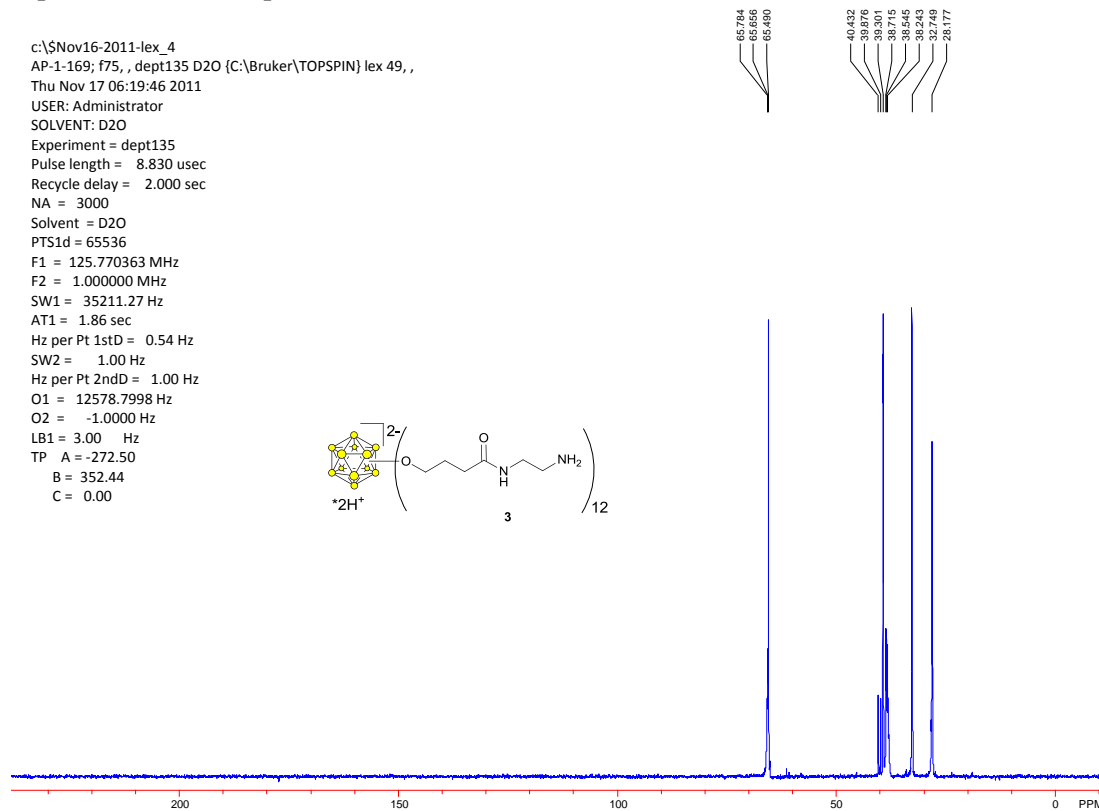
c:\Nov16-2011-lex_2
 AP-1-169; f75, , B11 D2O (C:\Bruker\TOPSPIN) lex 49, ,
 Wed Nov 16 15:56:34 2011
 USER: Administrator
 SOLVENT: D2O
 Experiment = zg
 Pulse length = 11.700 usec
 Recycle delay = 0.001 sec
 NA = 1024
 Solvent = D2O
 P1 = 4096
 F1 = 160.461578 MHz
 F2 = 1.000000 MHz
 SW1 = 64102.56 Hz
 AT1 = 0.06 sec
 Hz per Pt 1stD = 15.65 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = 0.0033 Hz
 O2 = -1.0000 Hz
 LB1 = 0.00 Hz
 TP A = 398.98
 B = -570.91
 C = 0.00



¹³C NMR of compound 3

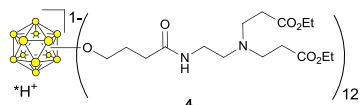


dept-135 NMR of compound 3



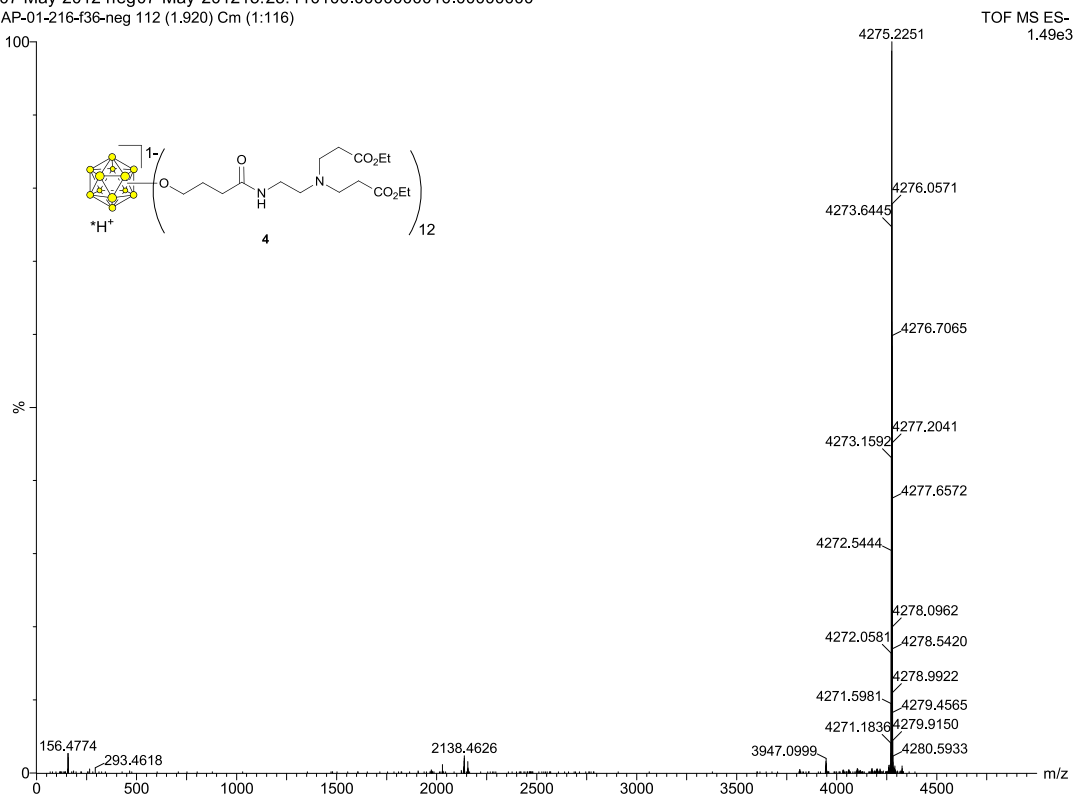
¹¹B NMR of compound 4

c:\Jan23-2012-lex_2
AP-1-181; D1+D2, , B11 CD3CN (C:\Bruker\TOPSPIN) lex 20, ,
Mon Jan 23 23:53:01 2012
USER: nmrsu
SOLVENT: CD3CN
Experiment = zg
Pulse length = 11.700 usec
Recycle delay = 0.001 sec
NA = 1024
Solvent = CD3CN
PTS1d = 4096
F1 = 160.461578 MHz
F2 = 1.000000 MHz
SW1 = 64102.56 Hz
AT1 = 0.06 sec
Hz per Pt 1stD = 15.65 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 0.0033 Hz
O2 = -1.0000 Hz
LB1 = 0.00 Hz
TP A = 503.75
B = -779.69
C = 0.00



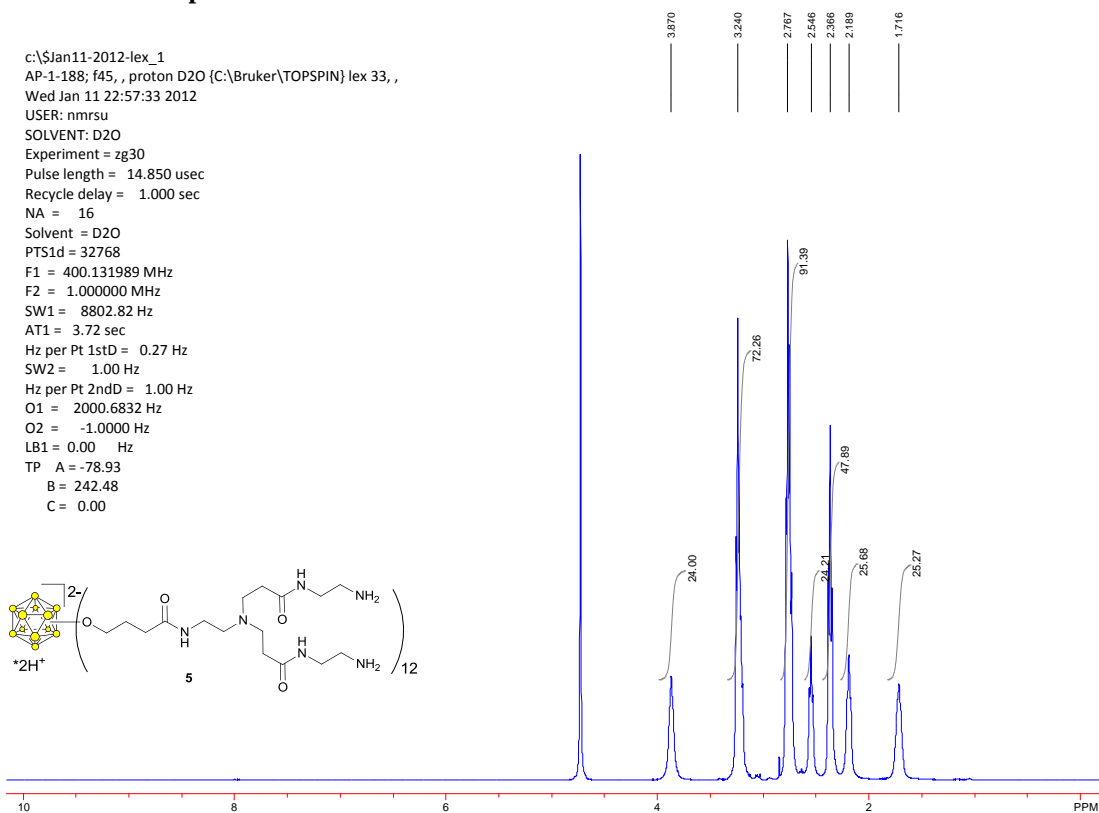
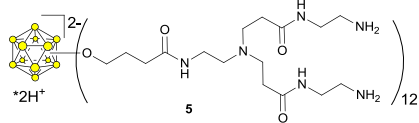
MS of compound 4

07 May 2012 neg07-May-201215:25:110100.000000010.00000000
AP-01-216-f36-neg 112 (1.920) Cm (1:116)



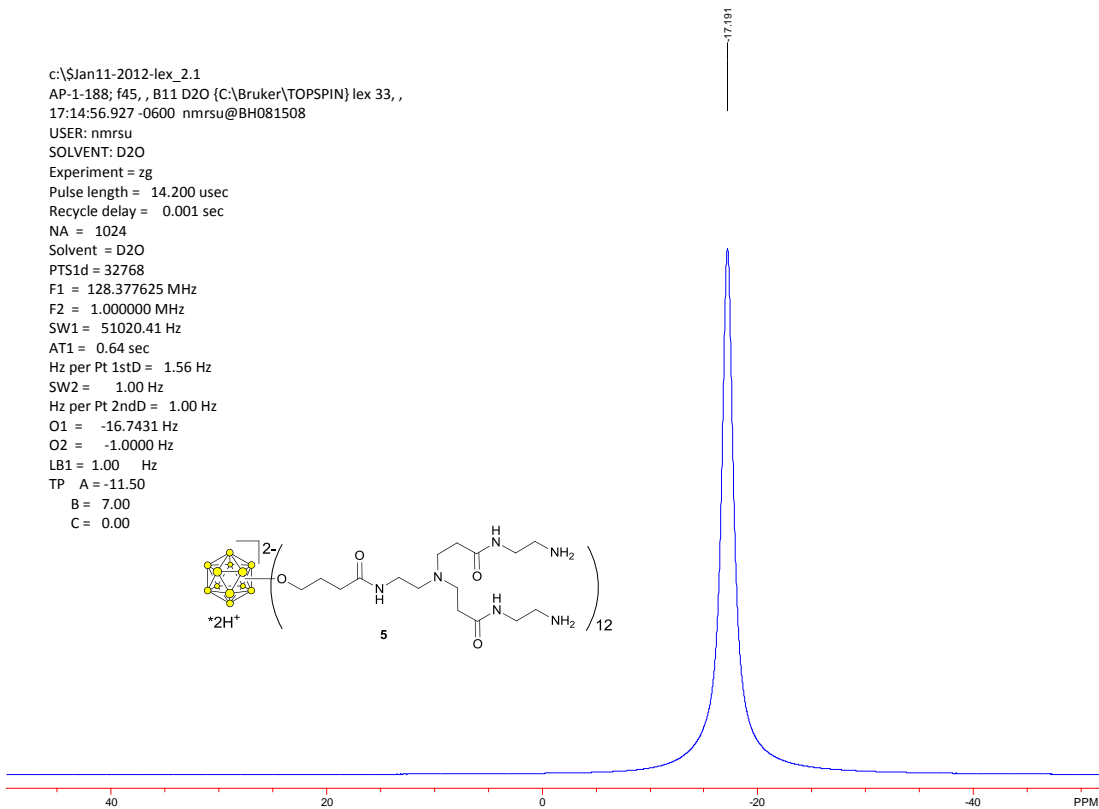
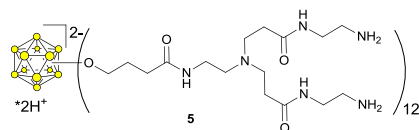
¹H NMR of compound 5

c:\Jan11-2012-lex_1
AP-1-188; f45, , proton D2O (C:\Bruker\TOPSPIN) lex 33, ,
Wed Jan 11 22:57:33 2012
USER: nmrsu
SOLVENT: D2O
Experiment = zg30
Pulse length = 14.850 usec
Recycle delay = 1.000 sec
NA = 16
Solvent = D2O
PTS1d = 32768
F1 = 400.131989 MHz
F2 = 1.000000 MHz
SW1 = 8802.82 Hz
AT1 = 3.72 sec
Hz per Pt 1stD = 0.27 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 2000.6832 Hz
O2 = -1.0000 Hz
LB1 = 0.00 Hz
TP A = -78.93
B = 242.48
C = 0.00

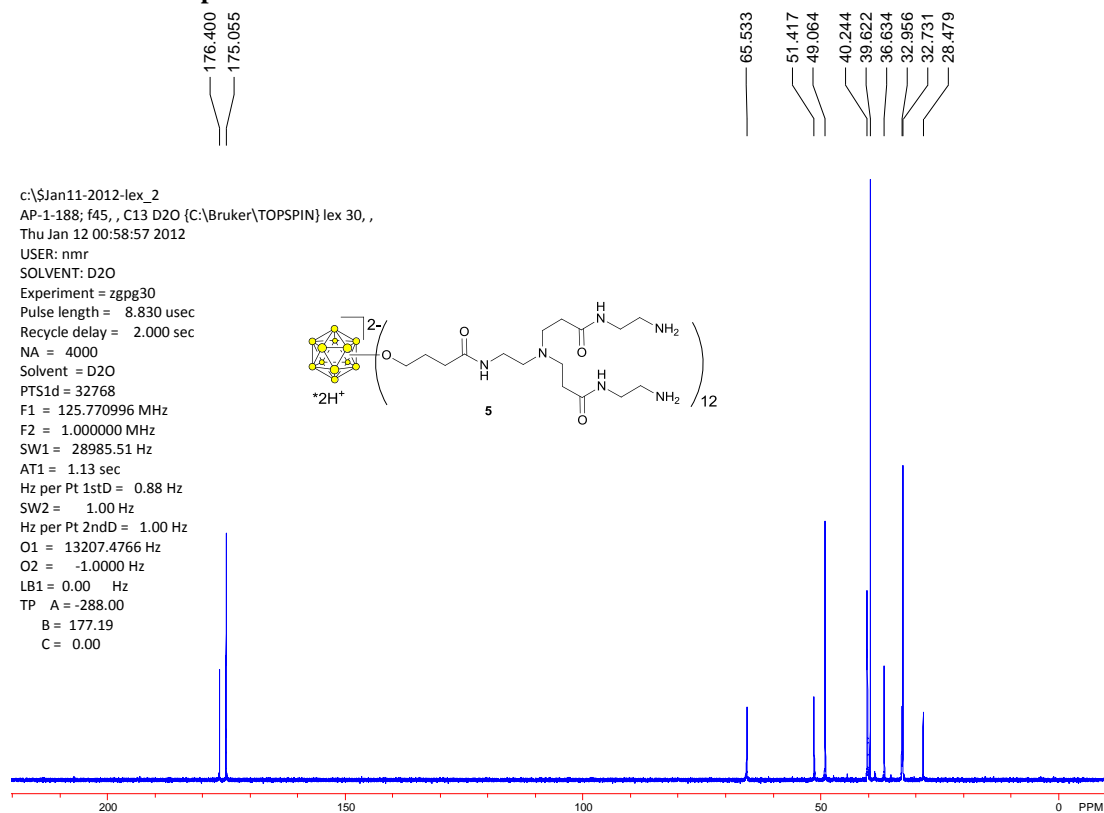


¹¹B NMR of compound 5

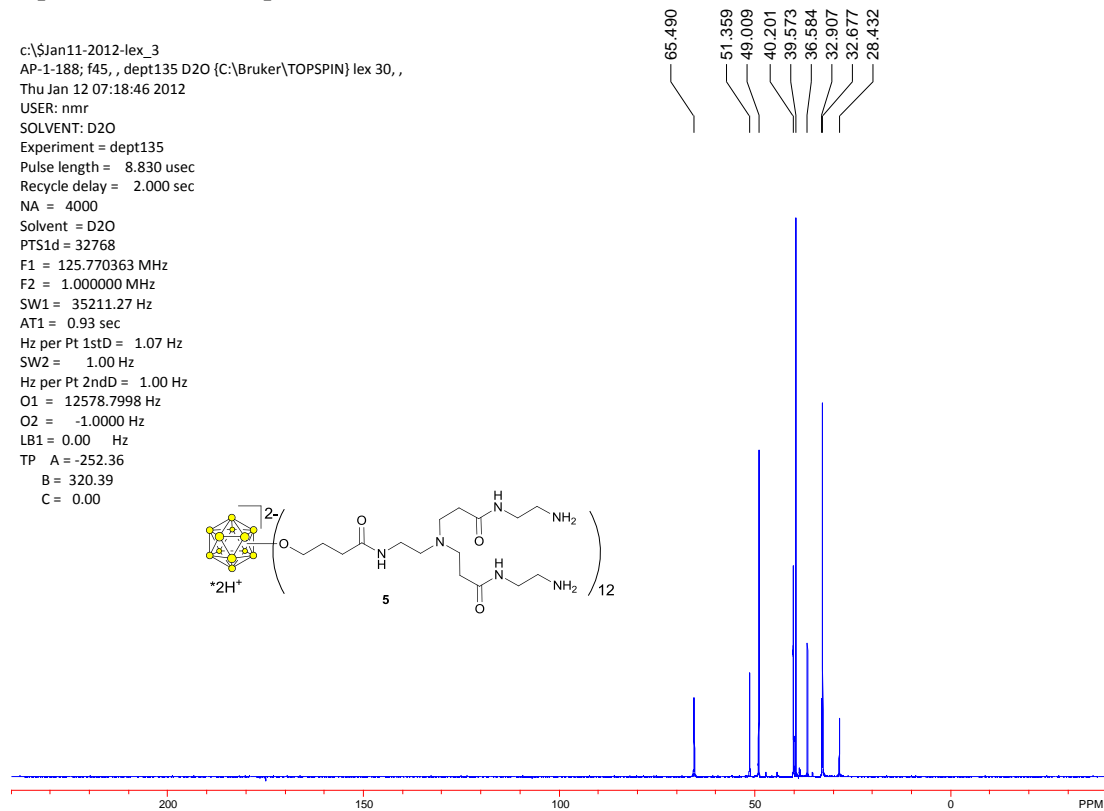
c:\Jan11-2012-lex_2.1
AP-1-188; f45, , B11 D2O (C:\Bruker\TOPSPIN) lex 33, ,
17:14:56.927-0600 nmrsu@BH081508
USER: nmrsu
SOLVENT: D2O
Experiment = zg
Pulse length = 14.200 usec
Recycle delay = 0.001 sec
NA = 1024
Solvent = D2O
PTS1d = 32768
F1 = 128.377625 MHz
F2 = 1.000000 MHz
SW1 = 51020.41 Hz
AT1 = 0.64 sec
Hz per Pt 1stD = 1.56 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = -16.7431 Hz
O2 = -1.0000 Hz
LB1 = 1.00 Hz
TP A = -11.50
B = 7.00
C = 0.00



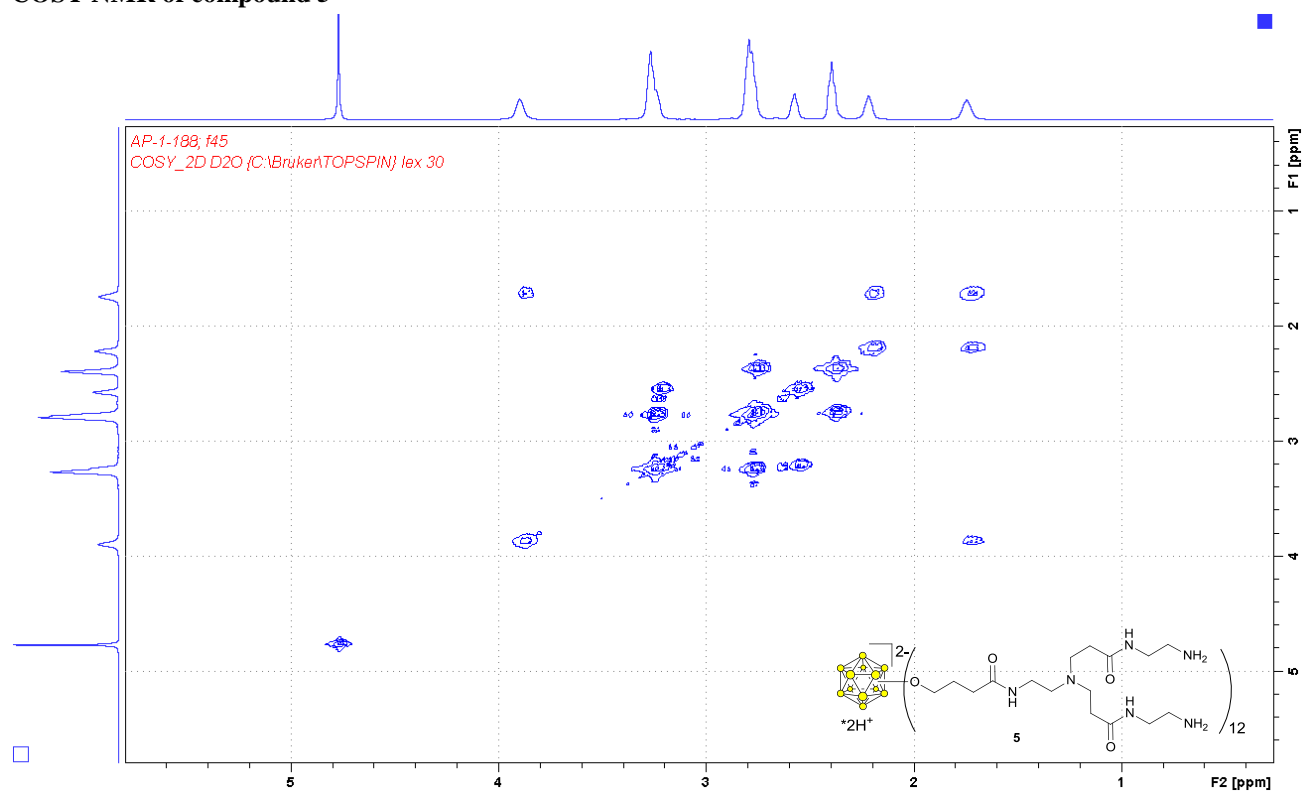
¹³C NMR of compound 5



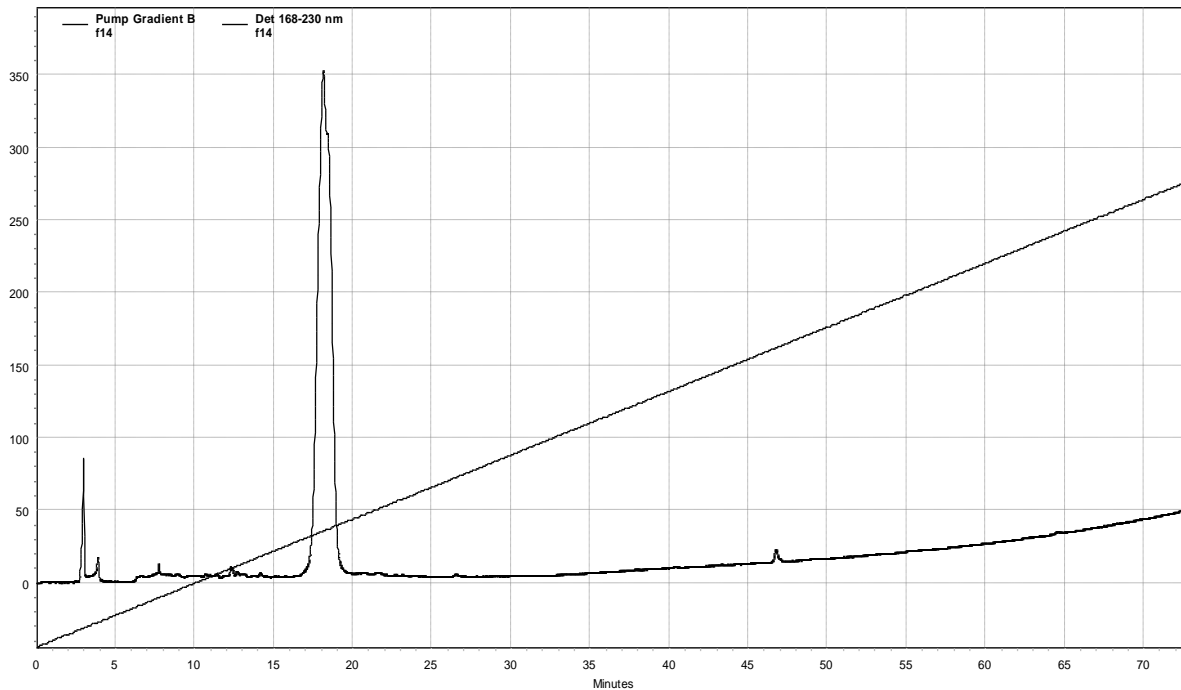
dept-135 NMR of compound 5



COSY NMR of compound 5



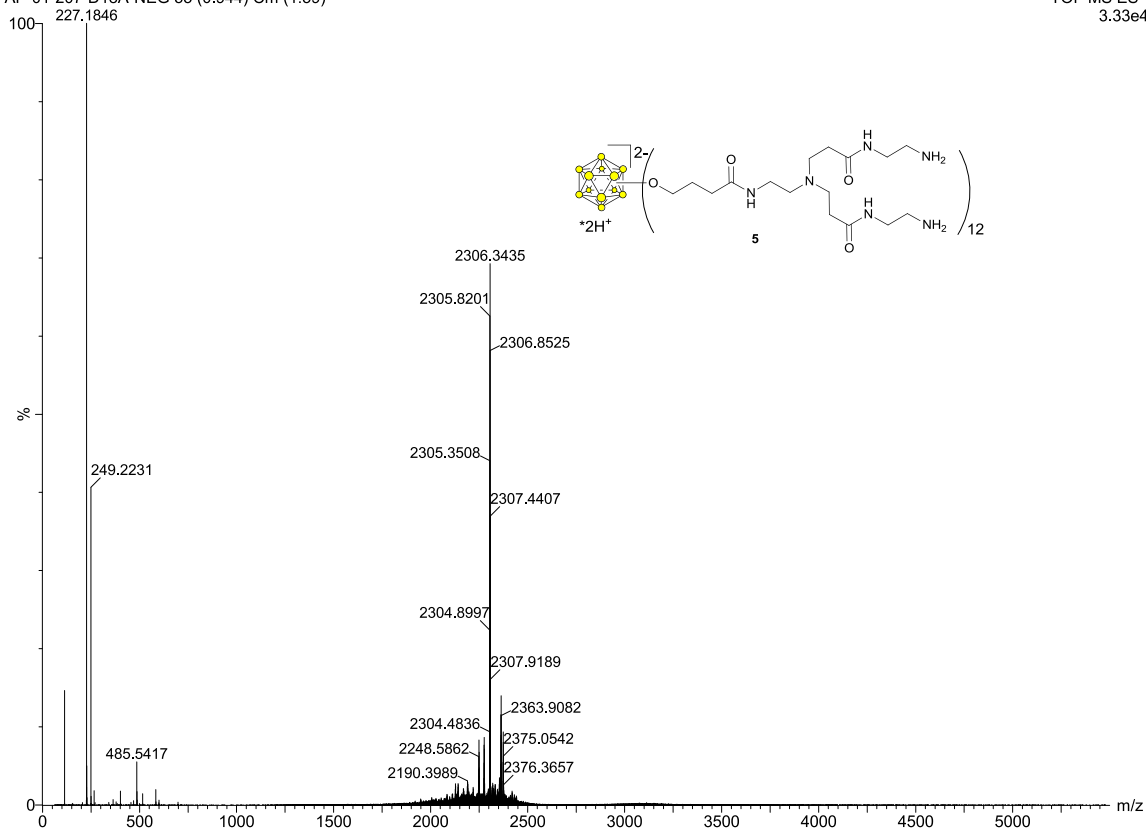
HPLC trace for compound 5



MS of compound 5

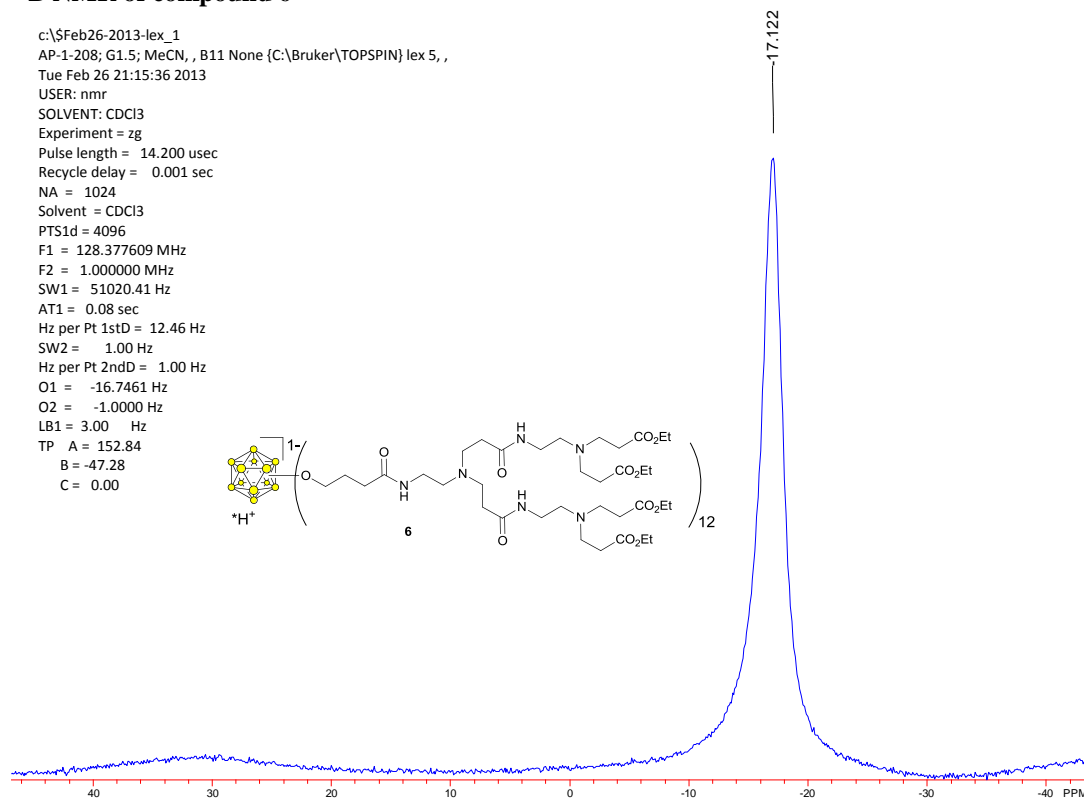
22 Mar 2012 neg22-Mar-201216:13:030100.0000000010.00000000
 AP-01-207-D18A-NEG 55 (0.944) Cm (1:59)

TOF MS ES-
 3.33e4



¹¹B NMR of compound 6

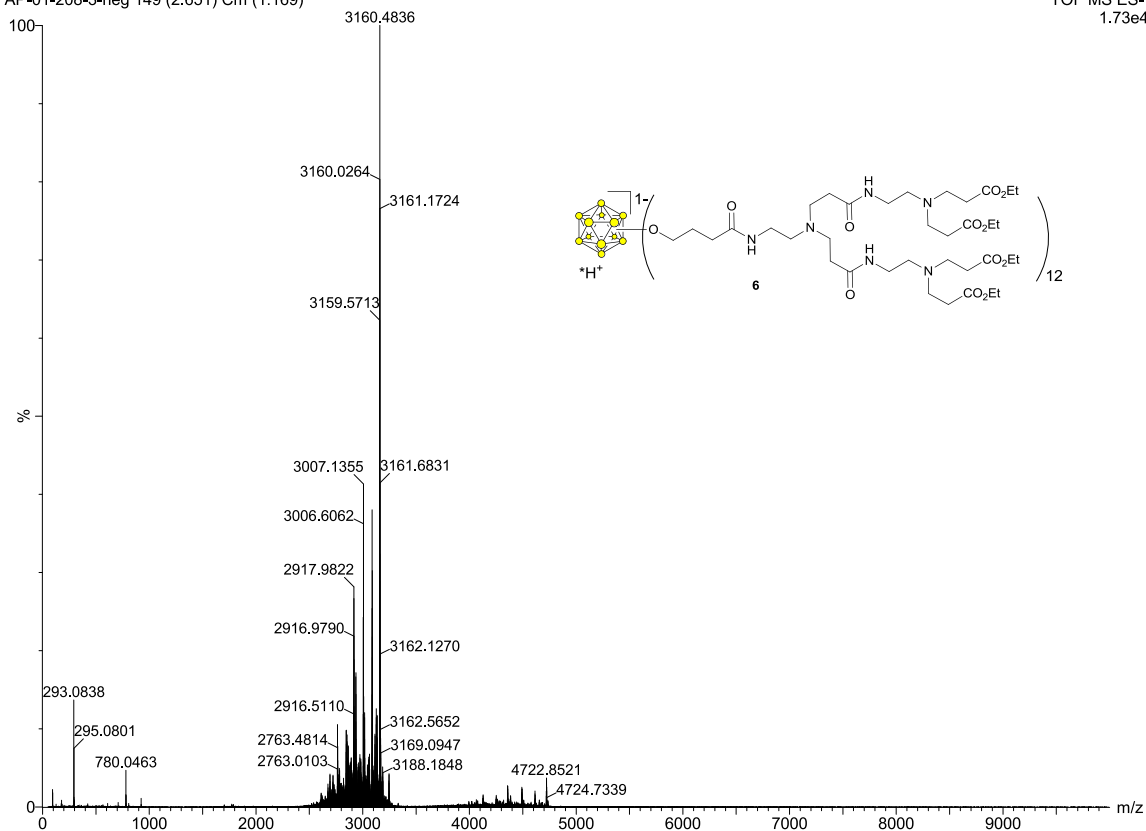
c:\\$Feb26-2013-lex_1
 AP-1-208; G1.5; MeCN, B11 None (C:\Bruker\TOPSPIN) lex 5, ,
 Tue Feb 26 21:15:36 2013
 USER: nmr
 SOLVENT: CDCl3
 Experiment = zg
 Pulse length = 14.200 usec
 Recycle delay = 0.001 sec
 NA = 1024
 Solvent = CDCl3
 PTS1d = 4096
 F1 = 128.377609 MHz
 F2 = 1.000000 MHz
 SW1 = 51020.41 Hz
 AT1 = 0.08 sec
 Hz per Pt 1stD = 12.46 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = -16.7461 Hz
 O2 = -1.0000 Hz
 LB1 = 3.00 Hz
 TP A = 152.84
 B = -47.28
 C = 0.00



MS of compound 6

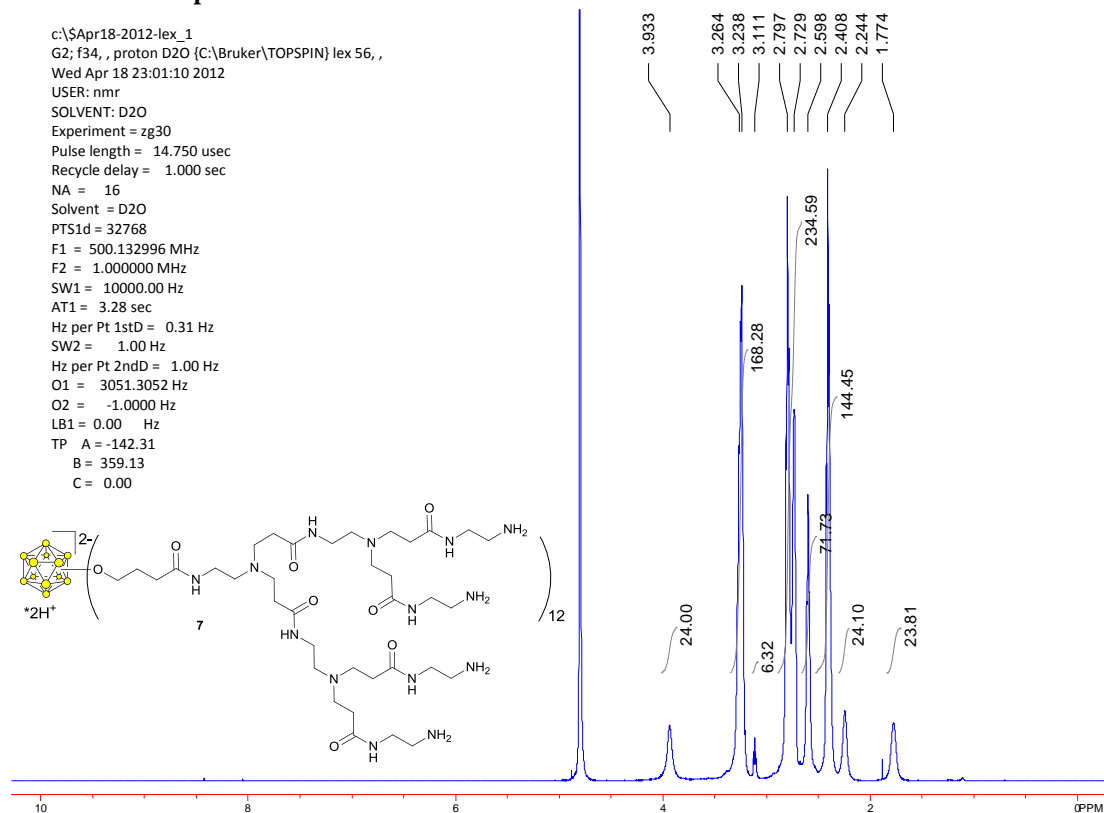
21 Mar 2012 neg21-Mar-201209:36:290100.0000000010.00000000
 AP-01-208-3-neg 149 (2.651) Cm (1:169)

TOF MS ES-
 1.73e4



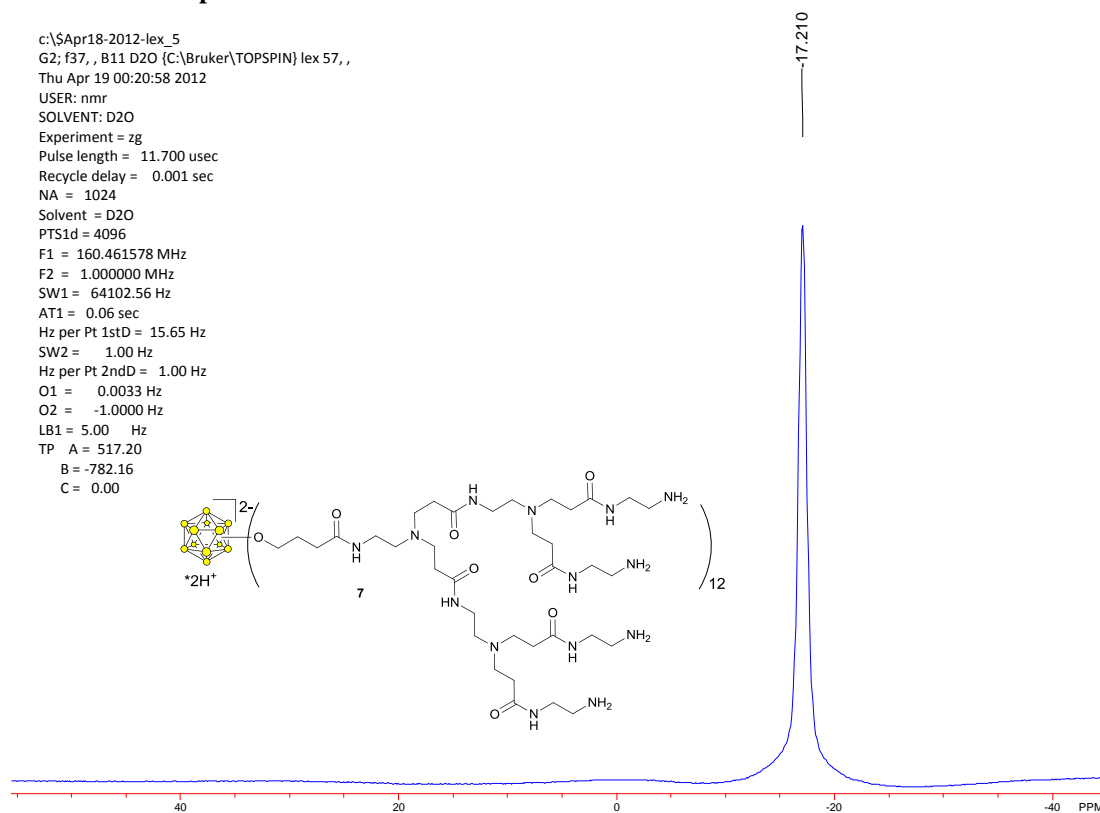
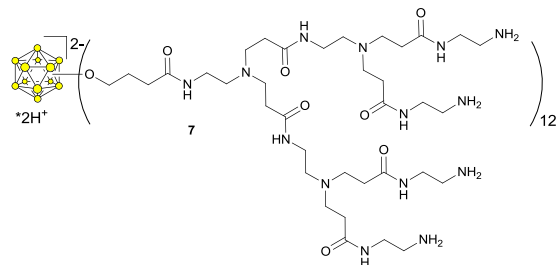
¹H NMR of compound 7

c:\\$Apr18-2012-lex_1
 G2; f34, , proton D2O (C:\Bruker\TOPSPIN) lex 56, ,
 Wed Apr 18 23:01:10 2012
 USER: nmr
 SOLVENT: D2O
 Experiment = zg30
 Pulse length = 14.750 usec
 Recycle delay = 1.000 sec
 NA = 16
 Solvent = D2O
 PTS1d = 32768
 F1 = 500.132996 MHz
 F2 = 1.000000 MHz
 SW1 = 10000.00 Hz
 AT1 = 3.28 sec
 Hz per Pt 1stD = 0.31 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = 3051.3052 Hz
 O2 = -1.0000 Hz
 LB1 = 0.00 Hz
 TP A = -142.31
 B = 359.13
 C = 0.00



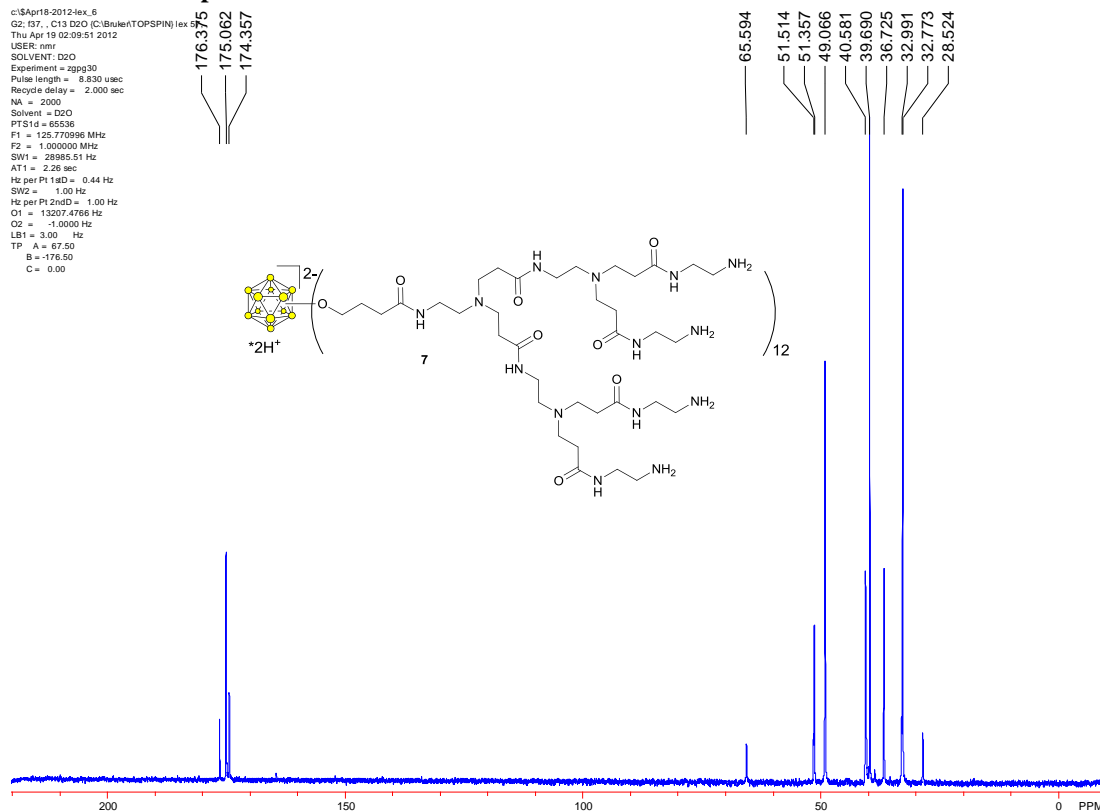
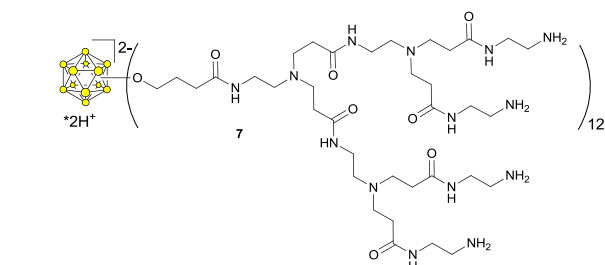
¹¹B NMR of compound 7

c:\\$Apr18-2012-lex_5
 G2; f37, , B11 D2O (C:\Bruker\TOPSPIN) lex 57, ,
 Thu Apr 19 00:20:58 2012
 USER: nmr
 SOLVENT: D2O
 Experiment = zg
 Pulse length = 11.700 usec
 Recycle delay = 0.001 sec
 NA = 1024
 Solvent = D2O
 PTS1d = 4096
 F1 = 160.461578 MHz
 F2 = 1.000000 MHz
 SW1 = 64102.56 Hz
 AT1 = 0.06 sec
 Hz per Pt 1stD = 15.65 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = 0.0033 Hz
 O2 = -1.0000 Hz
 LB1 = 5.00 Hz
 TP A = 517.20
 B = -782.16
 C = 0.00



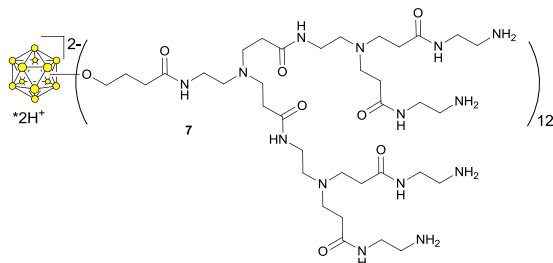
¹³C NMR of compound 7

c:\\$Apr18-2012-lex_6
 G2; f37, , C13 D2O (C:\Bruker\TOPSPIN) lex 57, ,
 Thu Apr 19 02:09:51 2012
 USER: nmr
 SOLVENT: D2O
 Experiment = zgpg30
 Pulse length = 8.830 usec
 Recycle delay = 2.000 sec
 NA = 2000
 Solvent = D2O
 PTS1d = 65536
 F1 = 125.770996 MHz
 F2 = 1.000000 MHz
 SW1 = 28985.51 Hz
 AT1 = 2.28 sec
 Hz per Pt 1stD = 0.44 Hz
 SW2 = 1.00 Hz
 Hz per Pt 2ndD = 1.00 Hz
 O1 = 13207.4766 Hz
 O2 = -1.0000 Hz
 LB1 = 3.00 Hz
 TP A = 67.50
 B = -176.50
 C = 0.00

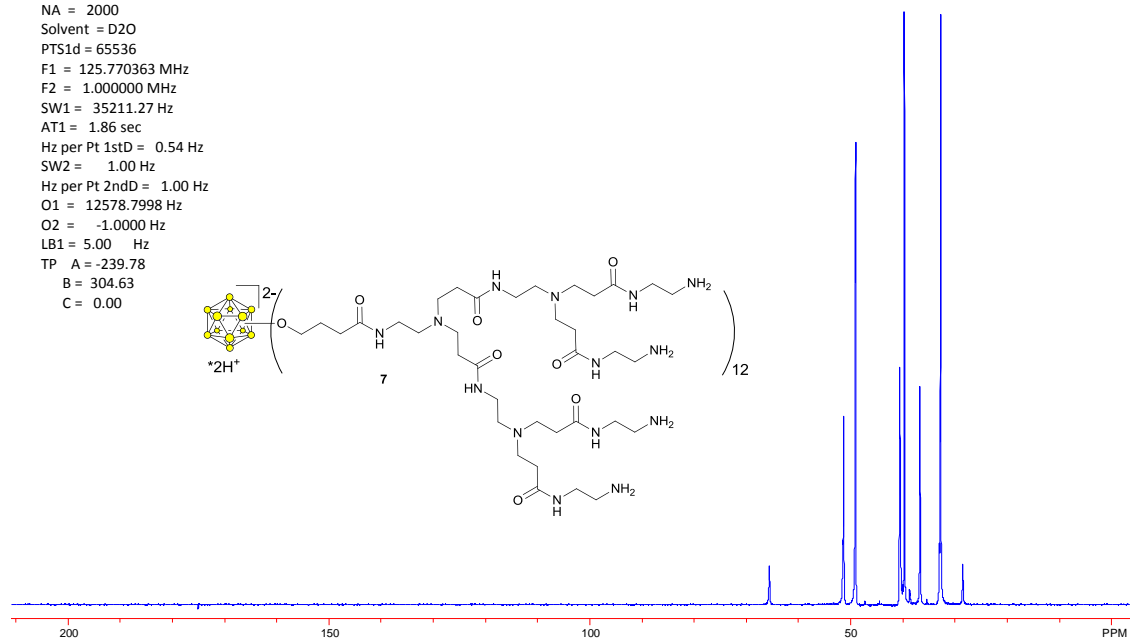


dept-135 NMR of compound 7

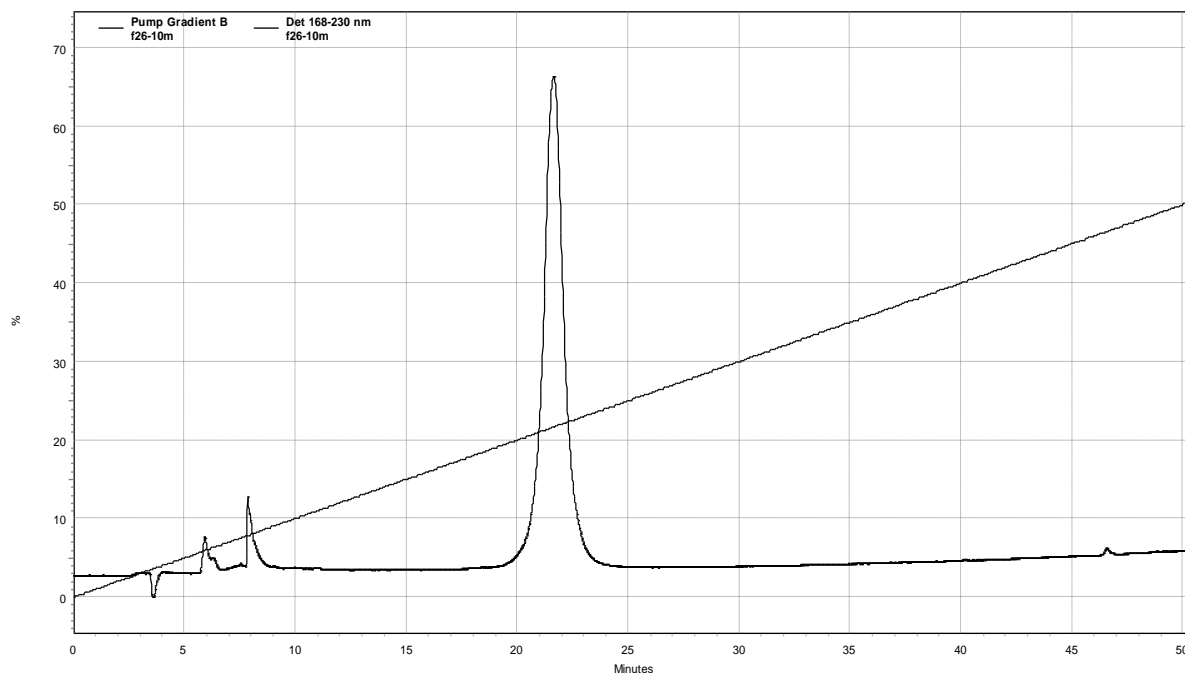
c:\\$Apr18-2012-lex_7
G2; f37, , dept135 D2O (C:\Bruker\TOPSPIN) lex 57, ,
Thu Apr 19 03:51:08 2012
USER: nmr
SOLVENT: D2O
Experiment = dept135
Pulse length = 8.830 usec
Recycle delay = 2.000 sec
NA = 2000
Solvent = D2O
PTS1d = 65536
F1 = 125.770363 MHz
F2 = 1.000000 MHz
SW1 = 35211.27 Hz
AT1 = 1.86 sec
Hz per Pt 1stD = 0.54 Hz
SW2 = 1.00 Hz
Hz per Pt 2ndD = 1.00 Hz
O1 = 12578.7998 Hz
O2 = -1.0000 Hz
LB1 = 5.00 Hz
TP A = -239.78
B = 304.63
C = 0.00



65.557
51.453
51.304
49.021
40.540
39.648
36.672
32.937
28.472



HPLC trace for compound 7



Mass spectrum deconvolution for 7 using the massXpert 2 software,³ [M] 10090.0172

11 Apr 2012 pos11-Apr-201213:55:49040.0000000010.00000000

AP-01-212-F34-POS 25 (0.458) Cm (1:166)

TOF MS ES+
2.25e4

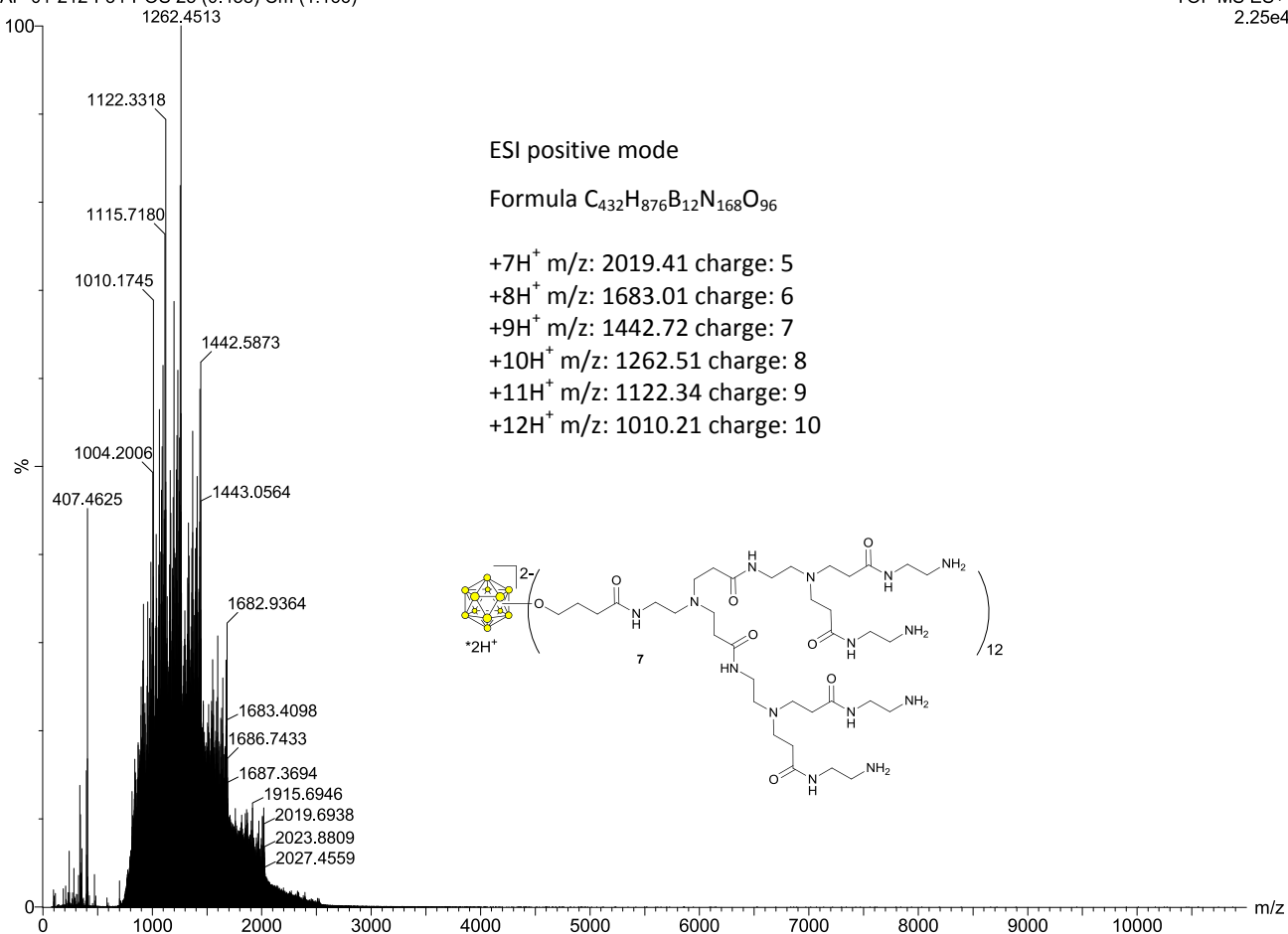
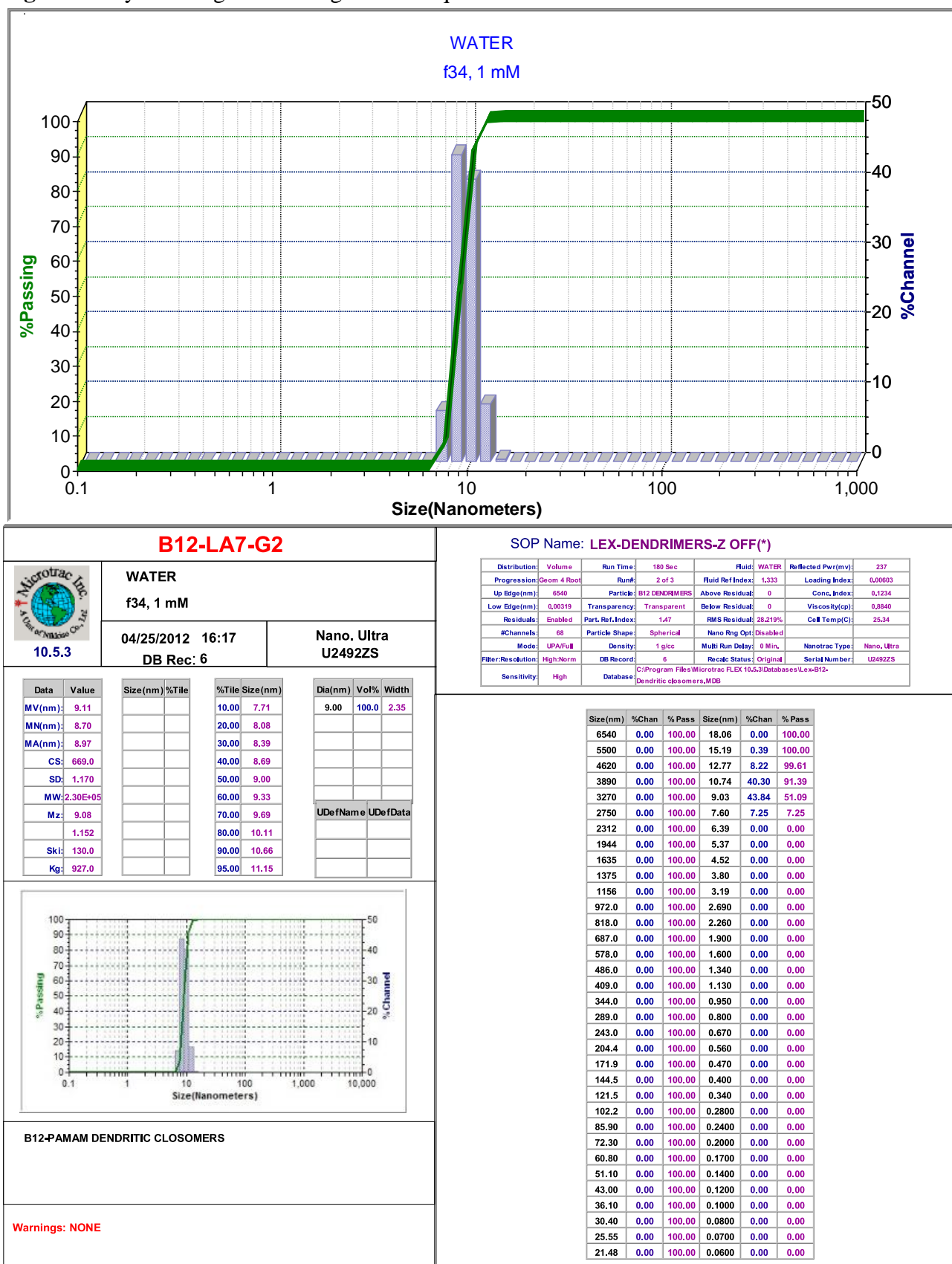


Figure S1 Dynamic light scattering data for aqueous solution of **7**



1. M. J. Bayer and M. F. Hawthorne, *Inorg. Chem.*, 2004, **43**, 2018-2020.
2. O. K. Farha, R. L. Julius, M. W. Lee, R. E. Huertas, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 2005, **127**, 18243-18251.
3. F. Rusconi, *Bioinformatics*, 2009, **25**, 2741-2742.