# Bismuth- and lead-texaphyrins: Towards potential α -core emitters for radiotherapy

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## - Supporting Information -

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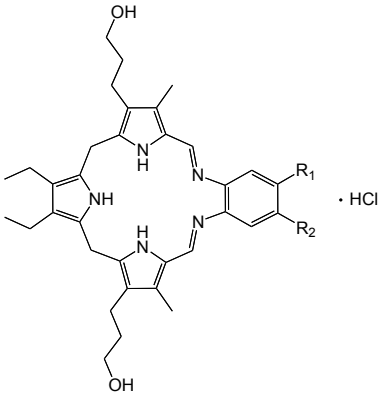
Experimental Section

All chemicals were obtained from commercial sources (Fisher Scientific, Acros Chemicals, Sigma-Aldrich or Strem Chemicals) and used as supplied unless otherwise noted. All solvents were of reagent grade quality. Fisher ailica gel (230-400 mesh, Grade 60 Å) and Sorbent Technologies alumina (neutral, standard activity I, 50-200 μm) were used for column chromatography. Thin layer chromatography (TLC) analyses were either performed on silica gel (aluminum backed, 200 μm or glass backed, 250 μm) or alumina neutral TLC plates (polyester backed, 200 μm), both obtained from Sorbent Technologies. All NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. Proton-NMR and $^{13}C$ NMR spectra used in the characterization of products were recorded on Varian Unity+ 300 MHz or Varian Mercury 400

MHz spectrometers. Chemical shifts are reported in units of δ (parts per million; ppm) and referenced to the residual solvent. Spectral splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Low and high resolution ESI mass spectra were obtained at the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at The University of Texas at Austin using a Thermo Finnigan LTQ instrument and a Qq FTICR (7 Tesla) instrument, respectively. UV-Vis spectra were recorded either on a Beckman DU 640B spectrophotometer or a Varian Cary 5000 UV-Vis spectrophotometer. HPLC spectra were taken on a Shimadzu High Performance Liquid Chromatograph (Fraction Collector Module FRC-10A, Auto Sampler SIL-20A, System Controller CBM-20A, UV/Vis Photodiode Array Detector SPD-M20A, Prominence).




$R_1 = R_2 =$ —$O(CH_2CH_2O)_3Me$ = $sp^3$-$Tex_{PEG}$

$R_1 = R_2 =$ —$OMe$ = $sp^3$-$Tex_{OMe}$

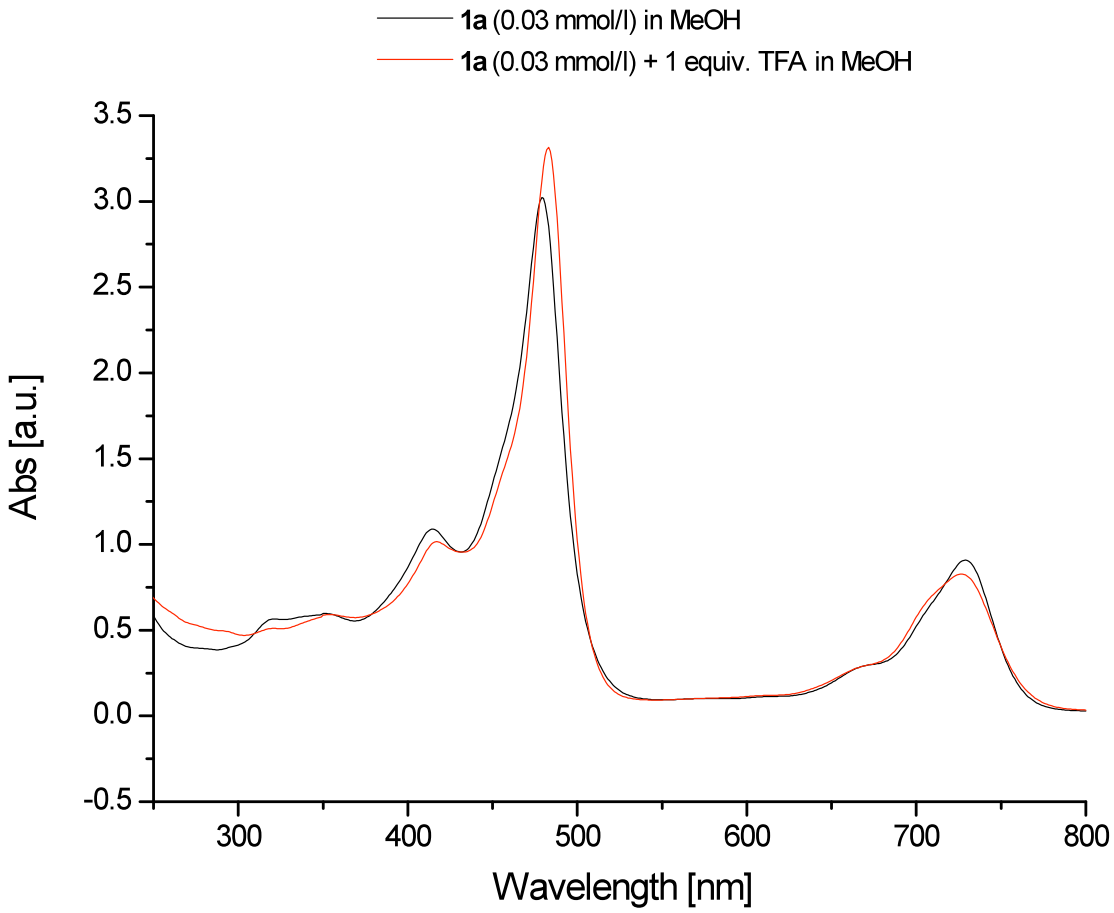
Macrocyclic, methylene-bridged texaphyrin precursor used to prepare MGd (generally referred to as $sp^3$-$Tex_{PEG}$) and the so-called $sp^3$ form of the analogous texaphyrin precursor with appended methoxy functionalities ($sp^3$-$Tex_{OMe}$); these compounds have been reported previously.[1-4]

## 1. Synthesis and Characterization of **1a**

The hydrochloride salt of $sp^3$-$Tex_{PEG}$ (189.8 mg, 216.2 mmol) was dissolved in 20 ml methanol. $Bi(NO_3)_3 \cdot 5H_2O$ (157.3 mg, 324.3 mmol, 1.5 equiv.) was added together with 1 ml triethylamine. The solution was stirred at 70 °C and gradually changed color from deep red to deep green. UV/Vis spectra were taken every 2 to 4 minutes (50 µL taken directly from the reaction mixture and diluted with 4 ml MeOH in the case of each sample). The insertion reaction was deemed over after 34 minutes. No further increase in the intensity of the Soret band was observed after that time, a finding interpreted in terms of the formation of the stable, aromatic texaphyrin scaffold being complete. The solvent was removed in vacuo and the residue was subjected to column chromatography (silica gel, first 90% $CH_2Cl_2$, then 10% MeOH, and then 25% $CH_2Cl_2$ and 75% MeOH, as the eluents). The deep green fraction was c4ollected and the solvent was removed in vacuo to give **1a** as a deep green crystalline material (152.0 mg, 64%).

| | |
|---|---|
| **UV/Vis** (MeOH, 25 °C): | λ [nm] = 480 (Soret-type band); 723 (Q-type band); |
| **$^1$H-NMR** (400 MHz, DMSO-$d_6$, 25 °C): | δ[ppm] = 1.74 (t, J = 7.2 Hz, 6H); 2.24 (q, J = 6.8 Hz, 4H); 3.23 (s, 6H), 3.45 (m, 4H); 3.49 (s, 6H); 3.58 (m, 4H); 3.66 (m, 8H), 3.82 (m, 4H); 3.93 (m, 8H); 4.16 (br t, J = 4 Hz, 4H); 4.95 (br t, J = 4 Hz, 2H); 9.76 (s, 2H); 10.30 (s, 2H); 12.93 (s, 2H); |
| **$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C): | δ[ppm] = 4.6 (2 C); 15.4 (2 C); 22.0 (2 C); 32.2 (2 C); 37.8 (2 C); 55.2 (2 C); 59.5 (2 C); 69.0 (2 C); 70.1 (2 C); 71.3 (2 C); 100.1 (2 C); 116.7 (2 C); 117.1 (2 C); 118.0 (2 C); 128.4 (2 C); 150.1 (2 C); 150.9 (2 C); 151.4 (2 C); 155.5 (2 C); |
| **Low Resolution MS** (ESI): | 1098.47 ($M^+$, monomeric Bi(III)-texaphyrin with axial hydroxide ligand) |
| **High Resolution MS** (ESI): | calculated for $C_{48}H_{67}N_5O_{11}Bi^{+1}$ = 1098.4641; found: 1098.46354 ($C_{48}H_{67}N_5O_{10}Bi^{+1}$, $M^+$) |

**UV/Vis spectrum** for **1a** and upon addition of TFA



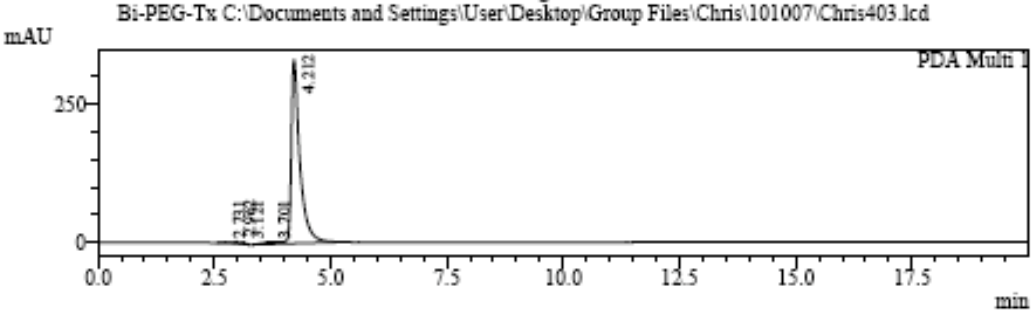
## **HPLC** and **UV/Vis spectrum** for **1a**

Sample Information

Sample Name : Bi-PEG-Tx

Chromatogram

Bi-PEG-Tx C:\Documents and Settings\User\Desktop\Group Files\Chris\101007\Chris403.lcd




1 PDA Multi 1 / 470nm 4nm

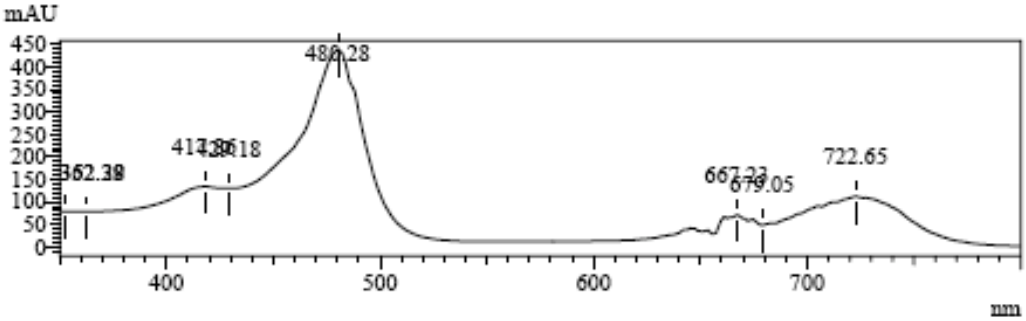
PeakTable

PDA Ch1 470nm 4nm

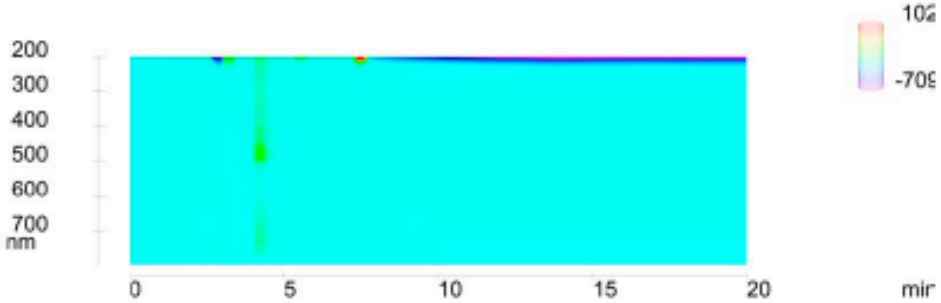
| Peak# | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 2.731 | 12838 | 0.291 |
| 2 | 2.962 | 34066 | 0.772 |
| 3 | 3.121 | 19495 | 0.442 |
| 4 | 3.701 | 101517 | 2.301 |
| 5 | 4.212 | 4244170 | 96.194 |
| Total | | 4412086 | 100.000 |

Spectrum

Peak# : 5
Retention Time : 4.212
Compound Name :
Spectrum Operation : None

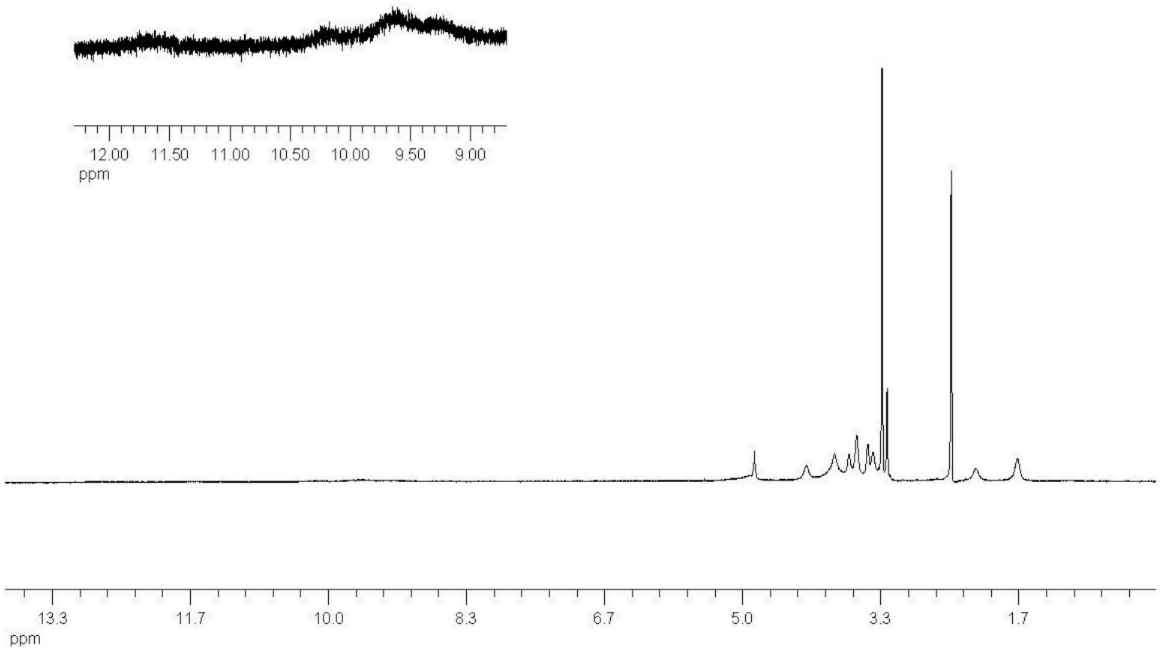



Contour



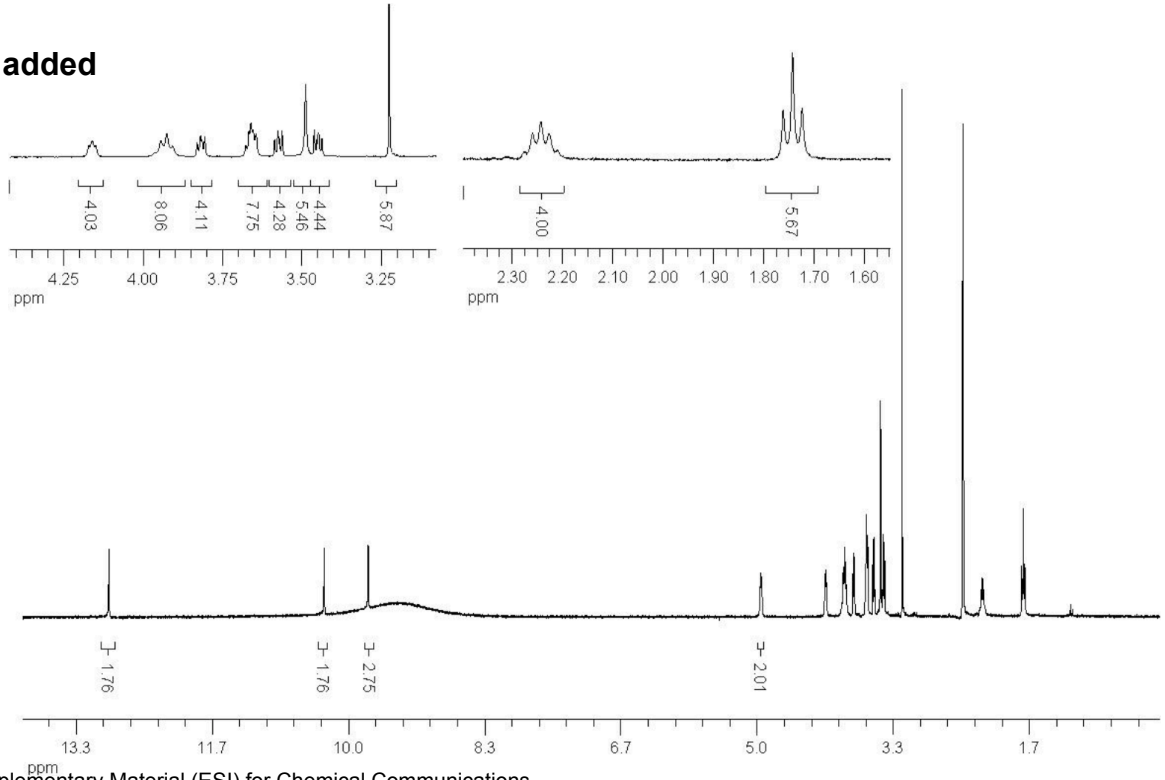
**$^1$H-NMR** (400 MHz, DMSO-$d_6$, 25 °C) for **1a**

## no TFA added

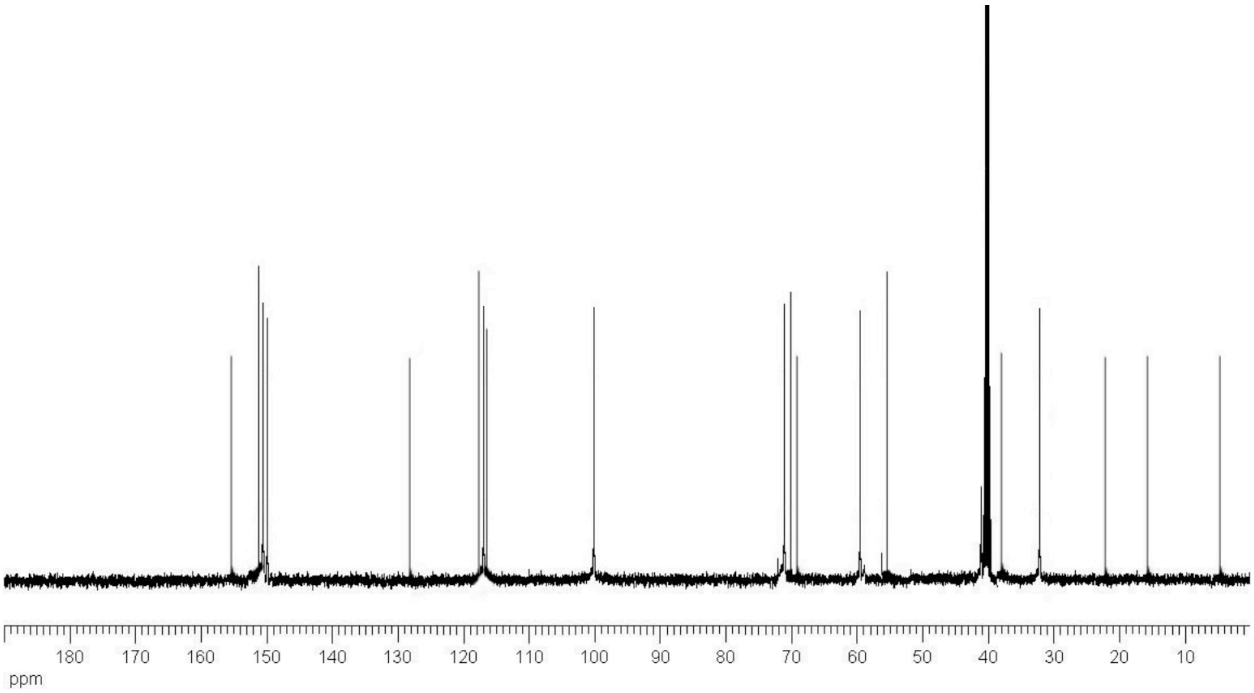



Upon addition of TFA (1 equiv.), the three signals for the protons on the sp$^2$-hybridized carbons appear as sharp singlets between 9.5 and 13 ppm.

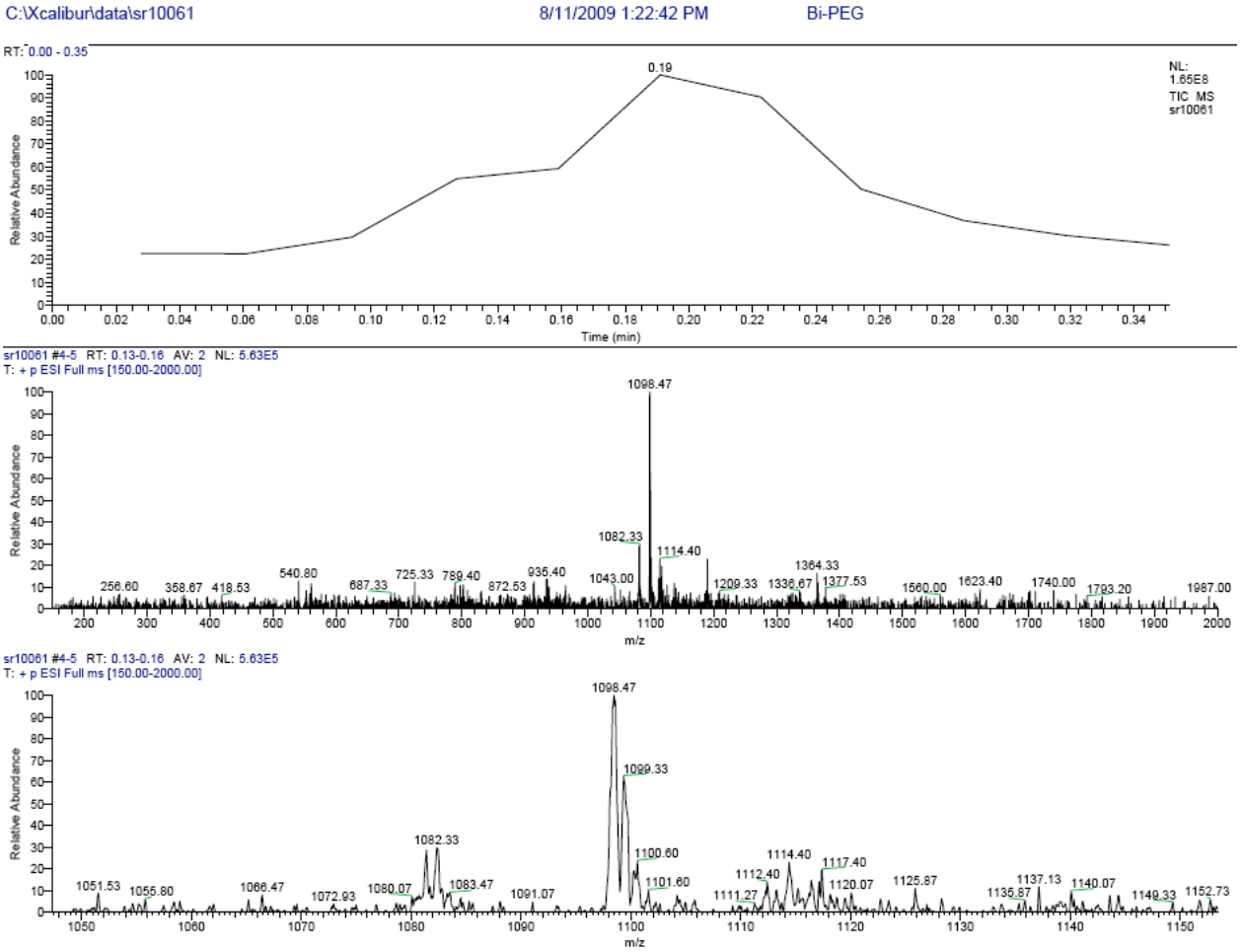
## TFA added



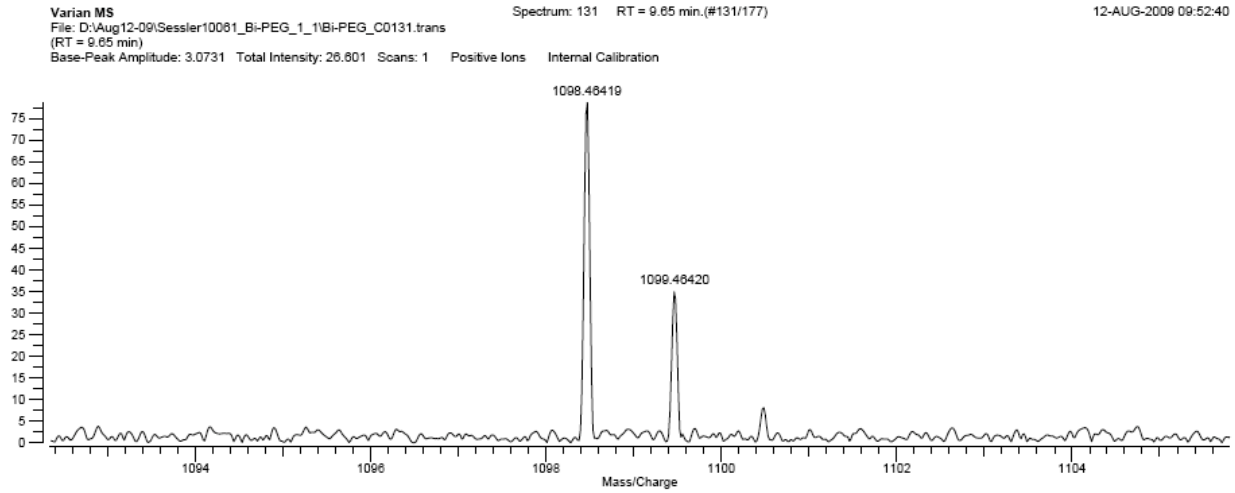
**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C) for **1a**



## **Low Resolution MS** (ESI) for **1a**



## **High Resolution MS** (ESI) for **1a**




# Elemental Composition Search Report:

**Target Mass:**

Target m/z = 1098.46419 ± .002
Charge = +1

**Possible Elements:**

| Element: | Exact Mass: | Min: | Max: |
|---|---|---|---|
| C | 12.000000 | 0 | 100 |
| H | 1.007825 | 0 | 120 |
| N | 14.003074 | 5 | 5 |
| O | 15.994915 | 11 | 11 |
| Bi | 208.980383 | 1 | 1 |

**Additional Search Restrictions:**

None

**Search Results:**

Number of Hits = 1

| m/z | Delta m/z | DBE | Formula |
|---|---|---|---|
| 1098.46354 | 0.00065 | 18.0 | $C_{48}H_{67}N_5O_{11}Bi^{+1}$ |

## 2. Synthesis and Characterization of **1b**

The hydrochloride salt of $sp^3$-$Tex_{PEG}$ (189.8 mg, 216.2 mmol) was dissolved in 20 ml methanol. $Pb(NO_3)_2$ (107.4 mg, 324.3 mmol, 1.5 equiv.) was added together with 1 ml triethylamine. The solution was stirred at 70 °C and gradually changed color from deep red to deep green. The mixture was stirred at that temperature for two hours. The solvent was removed in vacuo and the residue was then subjected to column chromatography (silica, first 90% $CH_2Cl_2$ and 10% MeOH, with the product slowly eluting with 25% $CH_2Cl_2$ and 75% MeOH). The deep green fraction was collected and the solvent was removed in vacuo to give **1b** as a deep green crystalline material (109.8 mg, 47%).

**UV/Vis** (MeOH, 25 °C): λ [nm] = 471 (Soret-type band); 743 (Q-type band);

**$^1$H-NMR** (400 MHz, $CD_3OD$, 25 °C): δ[ppm] = 1.57 (m, 6 H); 2.19 (br, 4 H); 3.27 (br, 6 H), 3.30 (m, 8 H); 3.50 (m, 4 H); 3.63 (m, 8 H); 3.74-3.95 (m, 16 H); 4.14 (br, 2H); 8.38 (s, 2 H); 8.98 (s, 2 H); 10.92 (br, 2 H);

**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C): δ[ppm] = 5.8 (2 C); 18.5 (2 C); 22.9 (2 C); 30.2 (2 C); 38.1 (2 C); 55.5 (2 C); 63.5 (2 C); 70.6 (2 C); 71.4 (2 C); 72.6 (2 C); 98.4 (2 C); 113.3 (2 C); 114.3 (2 C); 115.6 (2 C); 128.2 (2 C); 135.1 (2 C); 151.3 (2 C); 152.0 (2 C); 152.5 (2 C); 167.1 (2 C);

**MS** (ESI): 1080.40 ($M^+$, monomeric Pb-Tx, no axial ligand)

**High Resolution MS** (ESI): calculated for $C_{48}H_{66}N_5O_{10}Pb^{+1}$ = 1080.4576; found: 1080.45706 ($C_{48}H_{66}N_5O_{10}Pb^{+1}$, $M^+$)

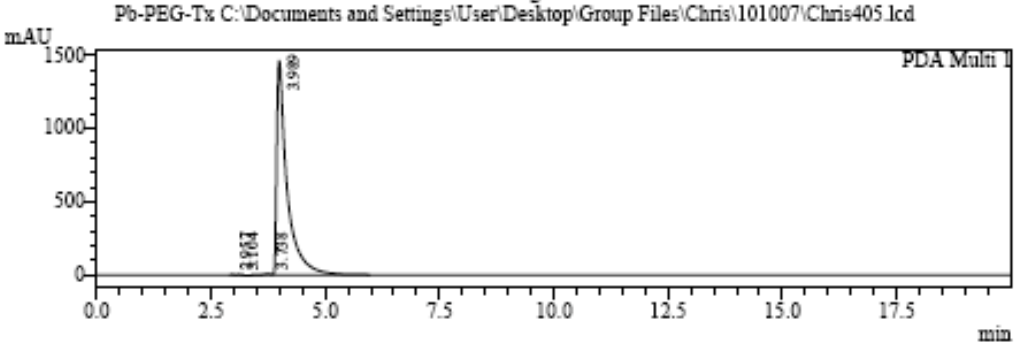
## **HPLC** and **UV/Vis spectrum** for **1b**

Sample Information

Sample Name : Pb-PEG-Tx

Chromatogram

Pb-PEG-Tx C:\Documents and Settings\User\Desktop\Group Files\Chris\101007\Chris405.lcd




1 PDA Multi 1 / 470nm 4nm

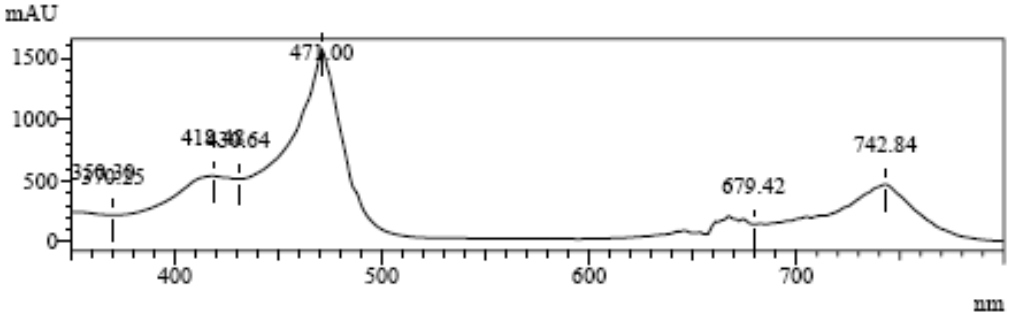
PeakTable

PDA Ch1 470nm 4nm

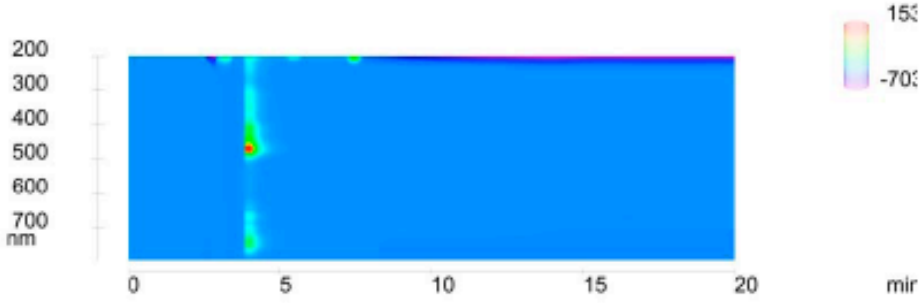
| Peak# | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 2.957 | 14580 | 0.062 |
| 2 | 3.104 | 19836 | 0.085 |
| 3 | 3.738 | 119072 | 0.510 |
| 4 | 3.989 | 23204431 | 99.343 |
| Total | | 23357920 | 100.000 |

Spectrum

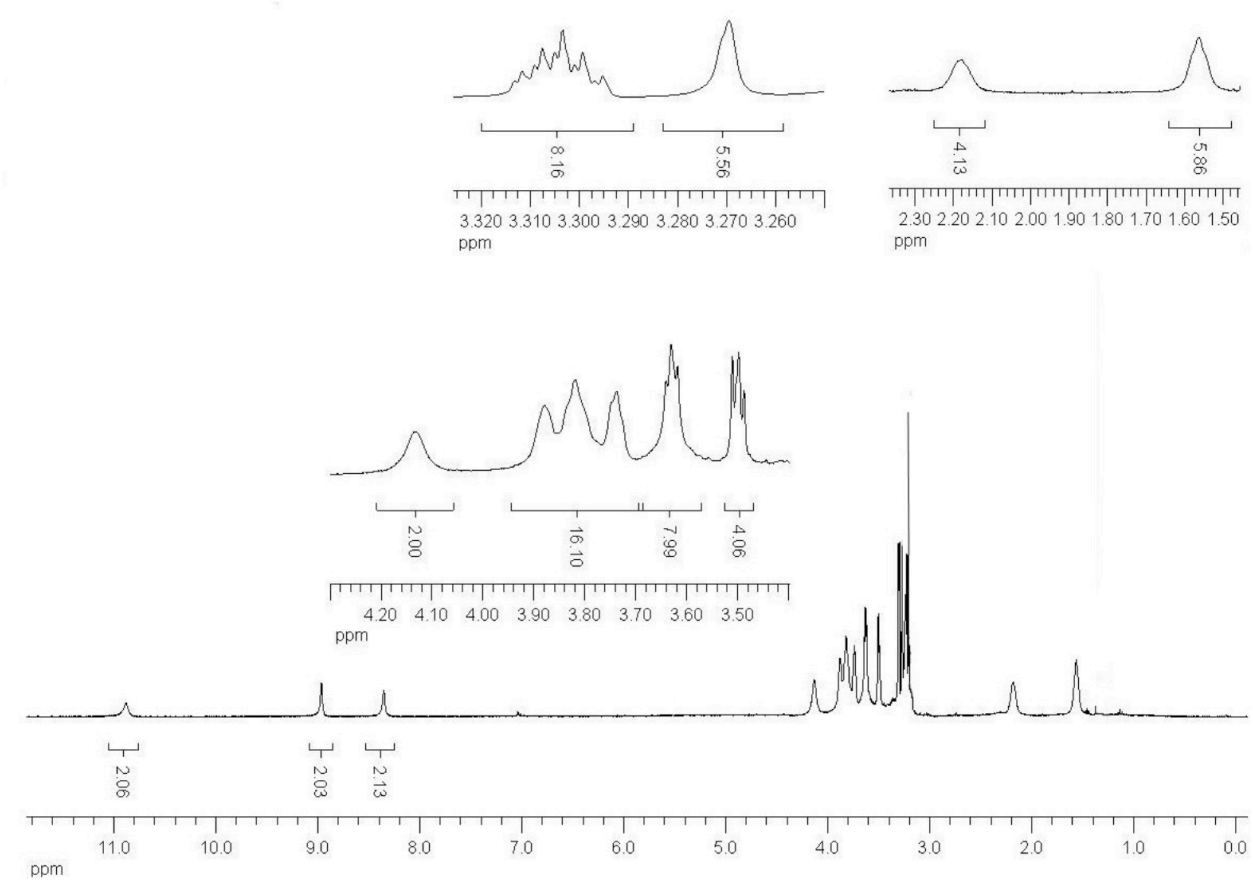
Peak# : 4
Retention Time : 3.989
Compound Name :
Spectrum Operation : None



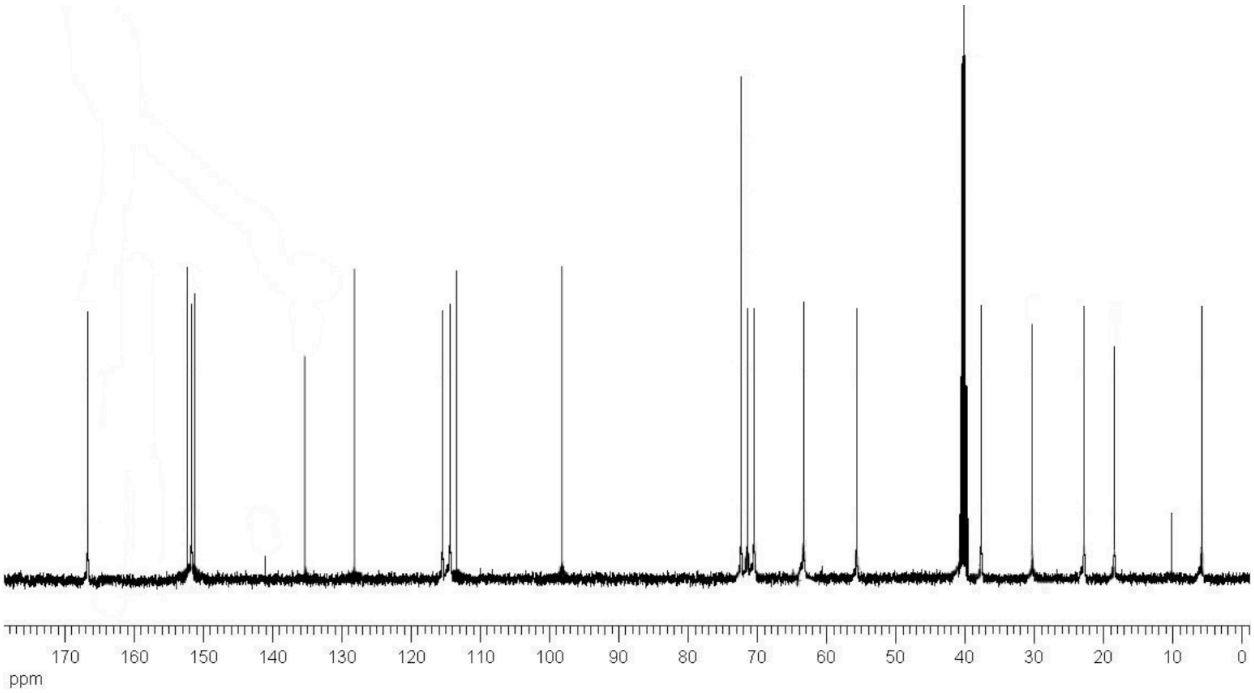

Contour



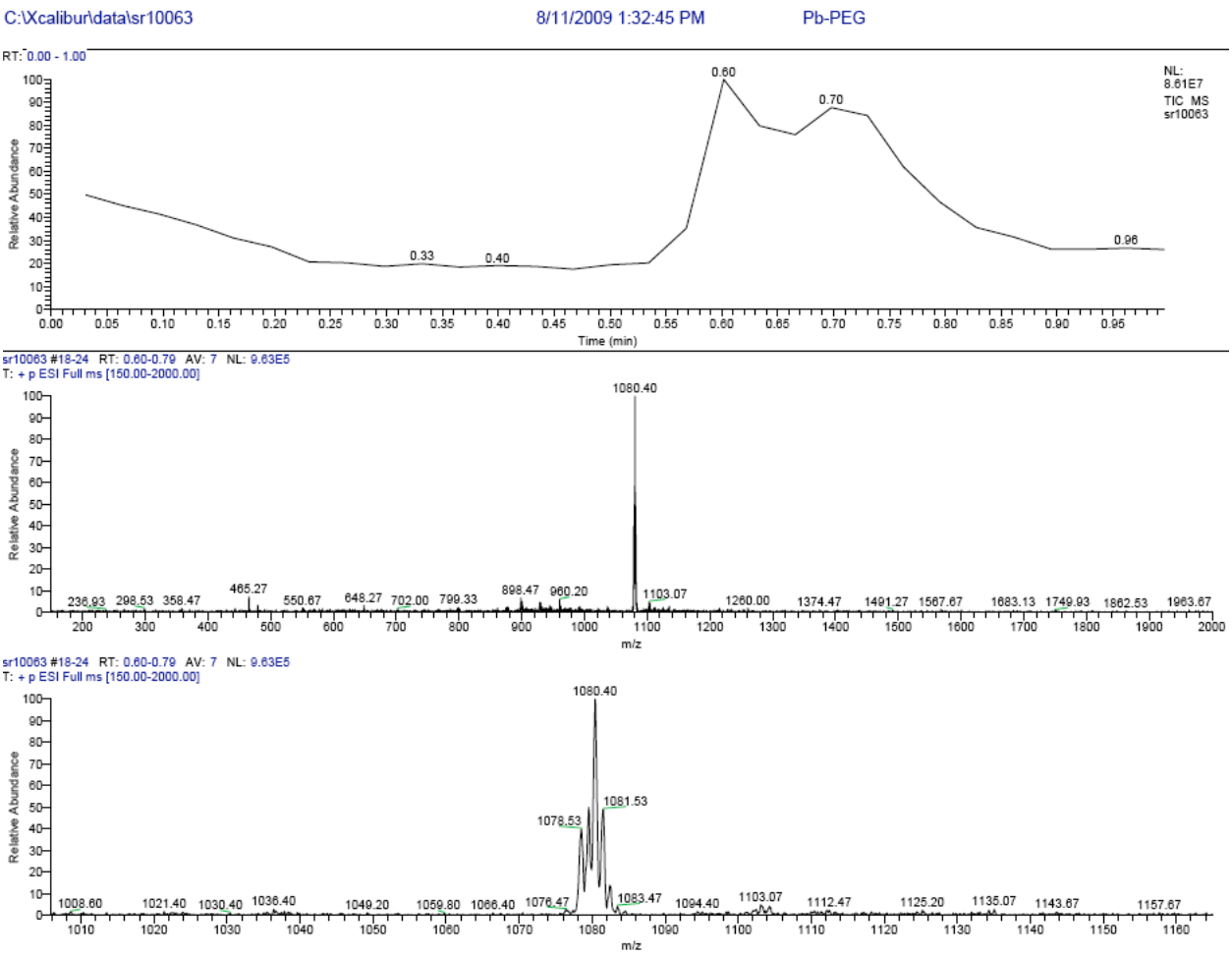
**$^1$H-NMR** (400 MHz, $CD_3OD$, 25 °C) for **1b**



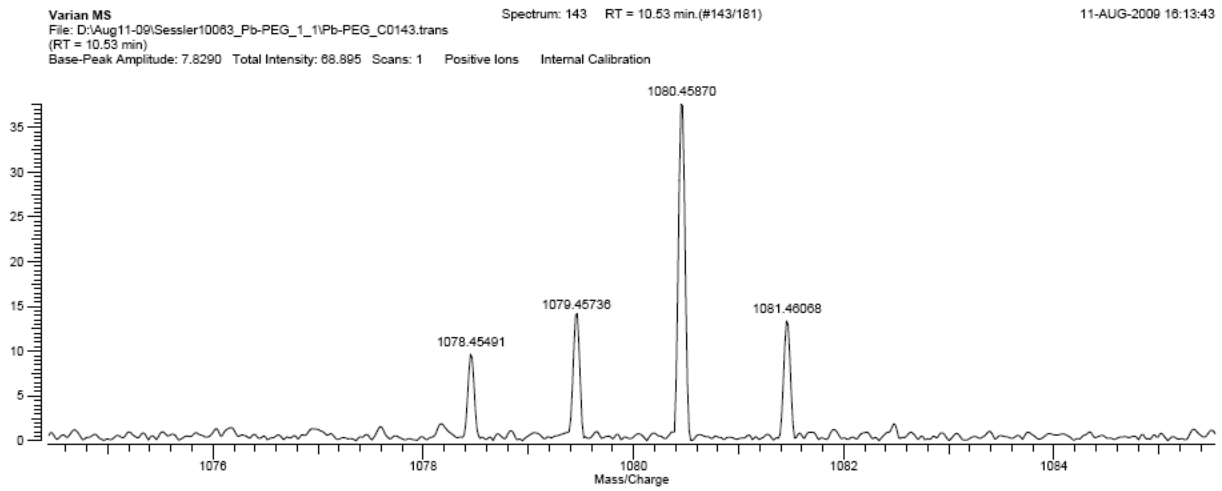
**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C) for **1b**



## **Low Resolution MS** (ESI) for **1b**



**High Resolution MS** (ESI) for **1b**




## Elemental Composition Search Report:

**Target Mass:**

Target m/z = 1080.45870 ± 0.004
Charge = +1

**Possible Elements:**

| Element: | Exact Mass: | Min: | Max: |
|---|---|---|---|
| C | 12.000000 | 0 | 100 |
| H | 1.007825 | 0 | 120 |
| N | 14.003074 | 5 | 5 |
| O | 15.994915 | 10 | 10 |
| Pb | 207.976636 | 1 | 1 |

**Additional Search Restrictions:**

None

**Search Results:**

Number of Hits = 1

| m/z | Delta m/z | DBE | Formula |
|---|---|---|---|
| 1080.45706 | 0.00164 | 18.5 | $C_{48}H_{66}N_5O_{10}Pb^{+1}$ |

## 3. Synthesis and Characterization of **2a**

The hydrochloride salt of $sp^3$-$Tex_{OMe}$ (140.6 mg, 216.2 mmol) was dissolved in 20 ml methanol. $Bi(NO_3)_3$ x $5H_2O$ (157.3 mg, 324.3 mmol, 1.5 equiv.) was added together with 1 ml triethylamine. The solution was stirred at 70 °C and gradually changed color from deep red to deep green. The mixture was stirred at that temperature for two hours. The solvent was removed in vacuo and the residue was then subjected to column chromatography (silica, first 95% $CH_2Cl_2$ and 5% MeOH, with the product then slowly eluting with 60% $CH_2Cl_2$ and 40% MeOH). The deep green fraction was collected and the solvent was removed in vacuo to give **2a** as a deep green crystalline material (129.9 mg, 72%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **2a** in methanol.

**UV/Vis** (MeOH, 25 °C): λ [nm] = 479 (Soret-type band); 722 (Q-type band);

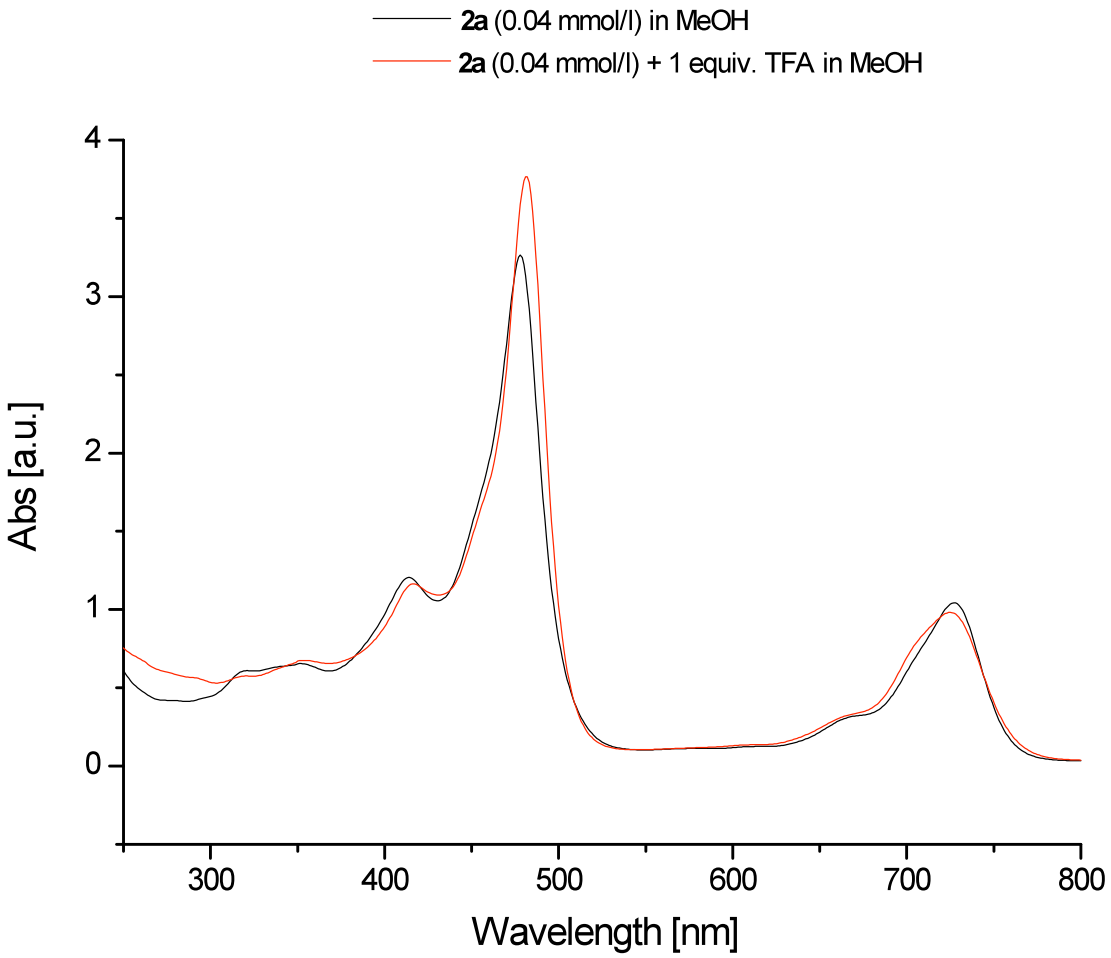
**$^1$H-NMR** (400 MHz, DMSO-$d_6$, 25 °C): δ[ppm] = 1.74 (t, J = 7.6 Hz, 6H); 2.25 (br t, J = 7.2 Hz, 4H); 3.16 (s, 2H), 3.51 (br s, 6H); 3.66 (t, J = 6 Hz, 4H); 3.95 (m, 6H); 4.45 (s, 6H); 9.77 (s, 2H); 10.35 (s, 2H); 13.01 (s, 2H);

**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C): δ[ppm] = 9.8 (2 C); 16.4 (2 C); 21.1 (2 C); 28.5 (2 C); 30.3 (2 C); 59.4 (2 C); 70.0 (2 C); 96.5 (2 C); 112.4 (2 C); 116.9 (2 C); 118.0 (2 C); 133.3 (2 C); 138.2 (2 C); 144.6(2 C); 145.5 (2 C); 146.8 (2 C); 158.3 (2 C);

**Low Resolution MS** (ESI): 834.27 ($M^+$, monomeric Bi(III)-texaphyrin with axial hydroxide ligand)

**High Resolution MS** (ESI): calculated for $C_{36}H_{43}N_5O_5Bi^{+1}$ = 834.3068; found: 834.30626 ($C_{48}H_{67}N_5O_{10}Bi^{+1}$, $M^+$)

**UV/Vis spectrum** for **2a** and upon addition of TFA



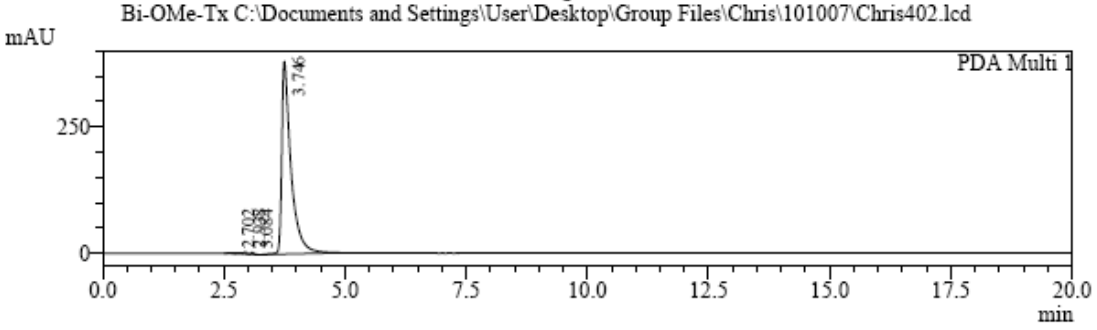
## **HPLC** and **UV/Vis spectrum** for **2a**

Sample Information

Sample Name : Bi-OMe-Tx

Chromatogram

Bi-OMe-Tx C:\Documents and Settings\User\Desktop\Group Files\Chris\101007\Chris402.lcd




1 PDA Multi 1 / 470nm 4nm

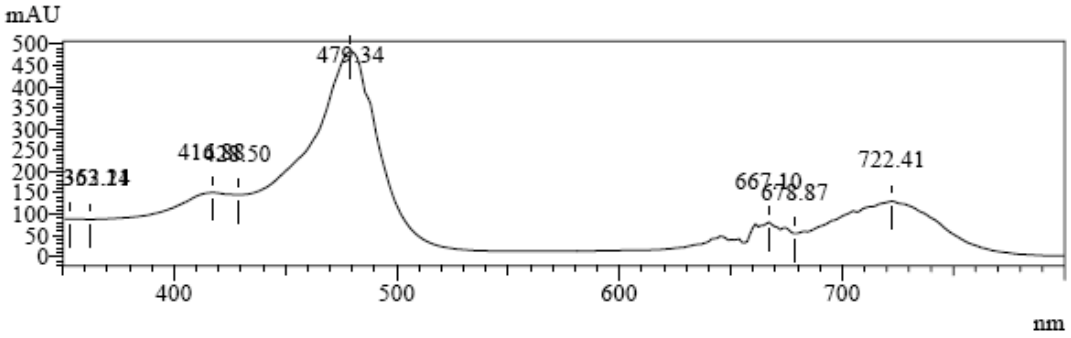
PeakTable

PDA Ch1 470nm 4nm

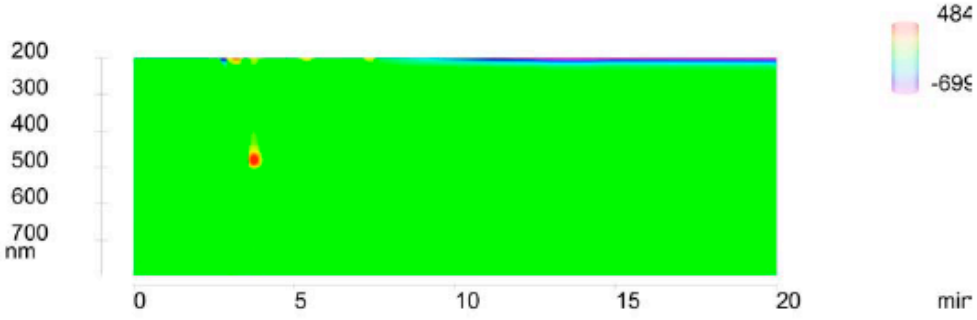
| Peak# | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 2.702 | 14837 | 0.291 |
| 2 | 2.938 | 30182 | 0.593 |
| 3 | 3.084 | 15542 | 0.305 |
| 4 | 3.746 | 5032730 | 98.811 |
| Total | | 5093291 | 100.000 |

Spectrum

Peak# : 4
Retention Time : 3.746
Compound Name :
Spectrum Operation : None

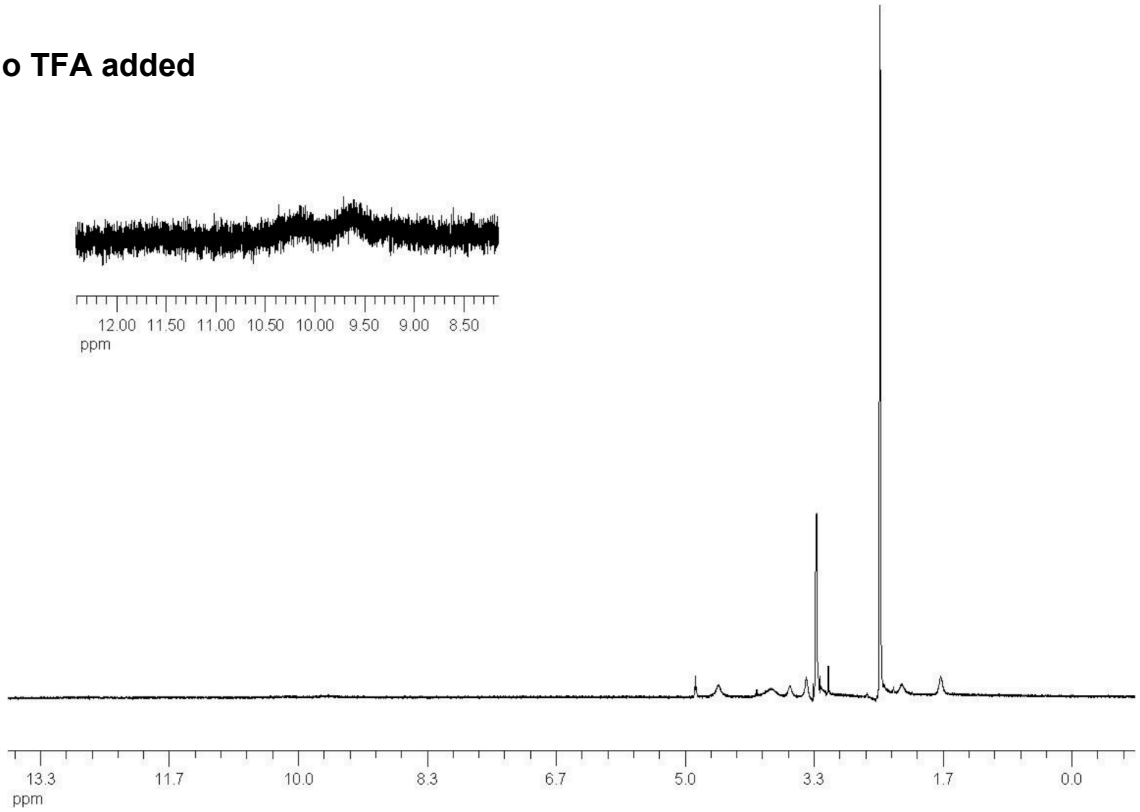



Contour



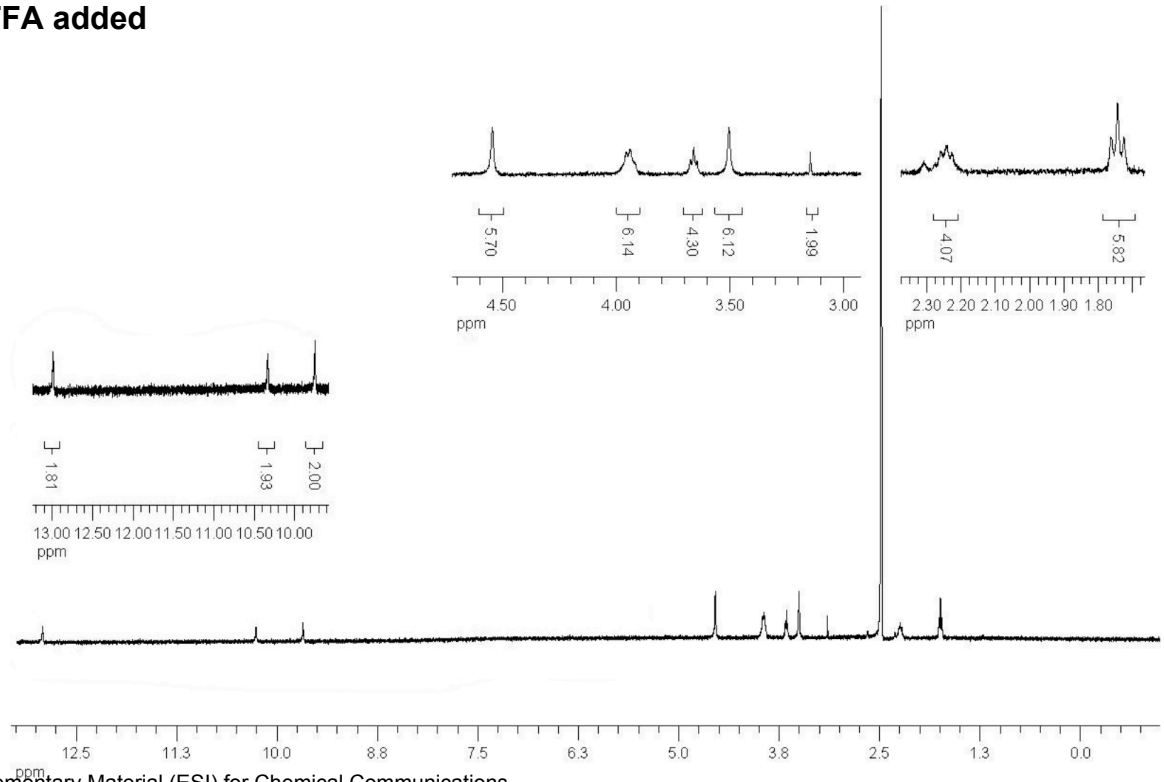
**$^1$H-NMR** (400 MHz, DMSO-$d_6$, 25 °C) for **2a**

**No TFA added**

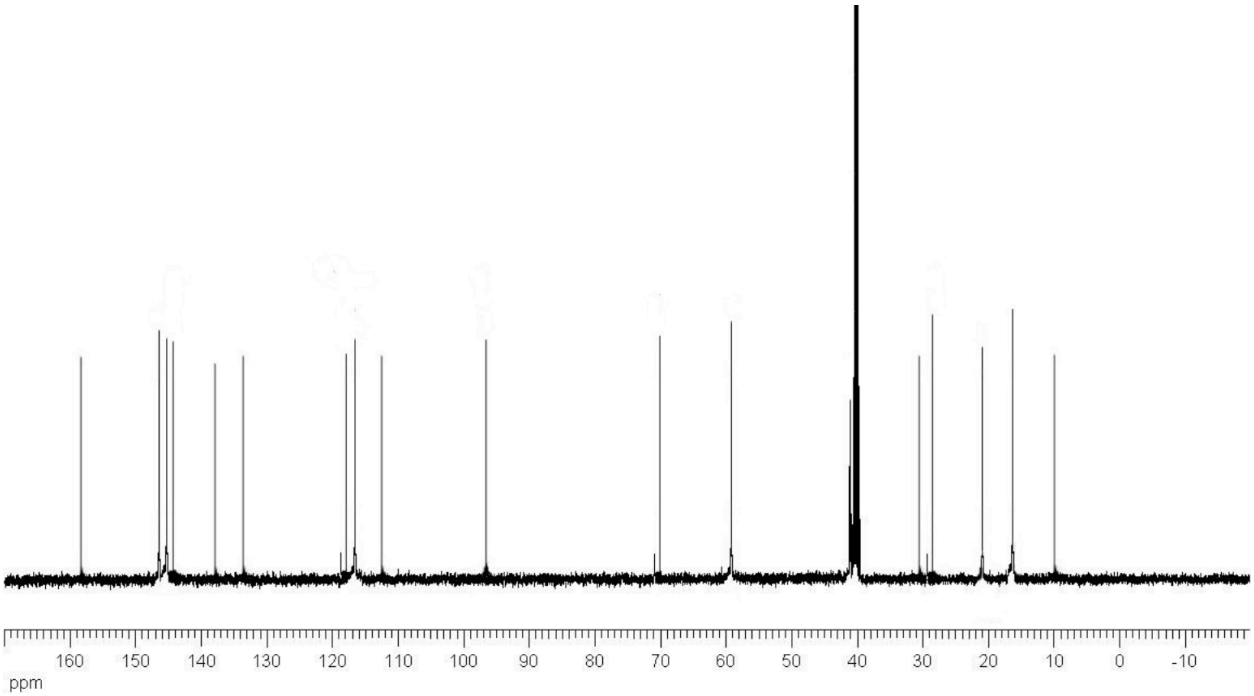



Upon addition of TFA (1 equiv.), the three signals for the protons on the sp$^2$-hybridized carbons appear as sharp singlets between 9.5 and 13 ppm.

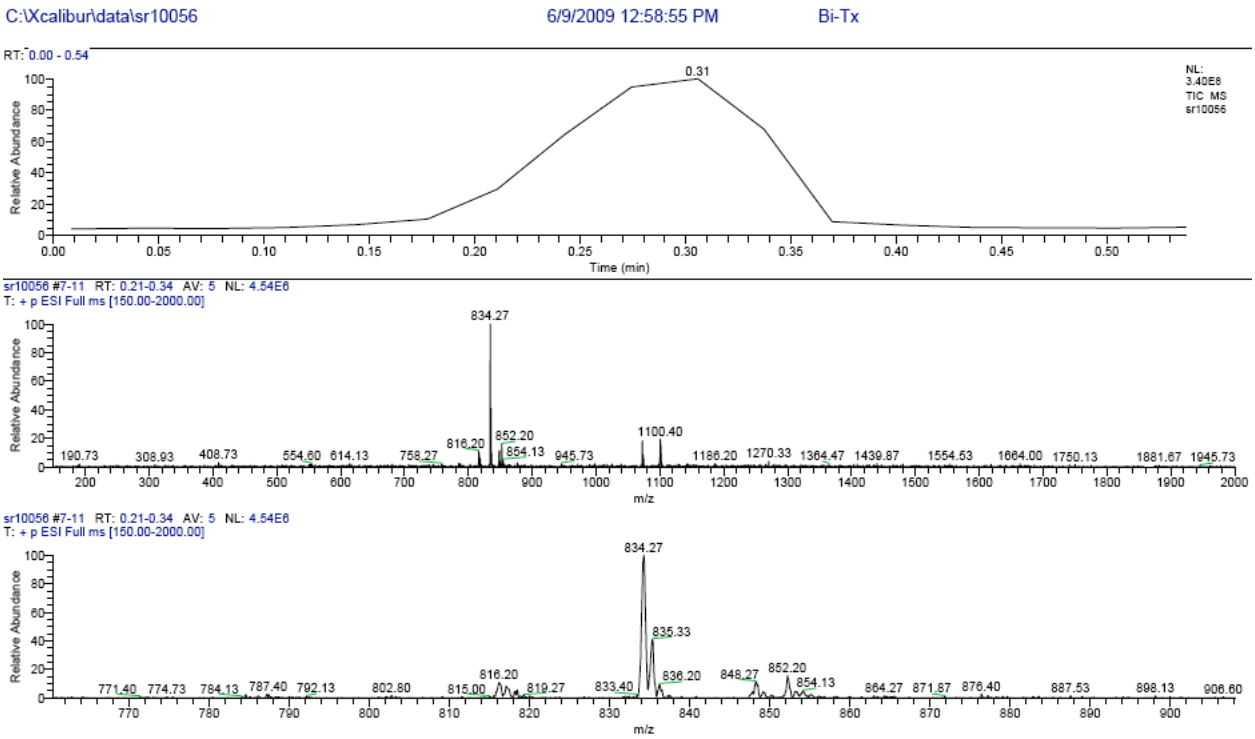
**TFA added**



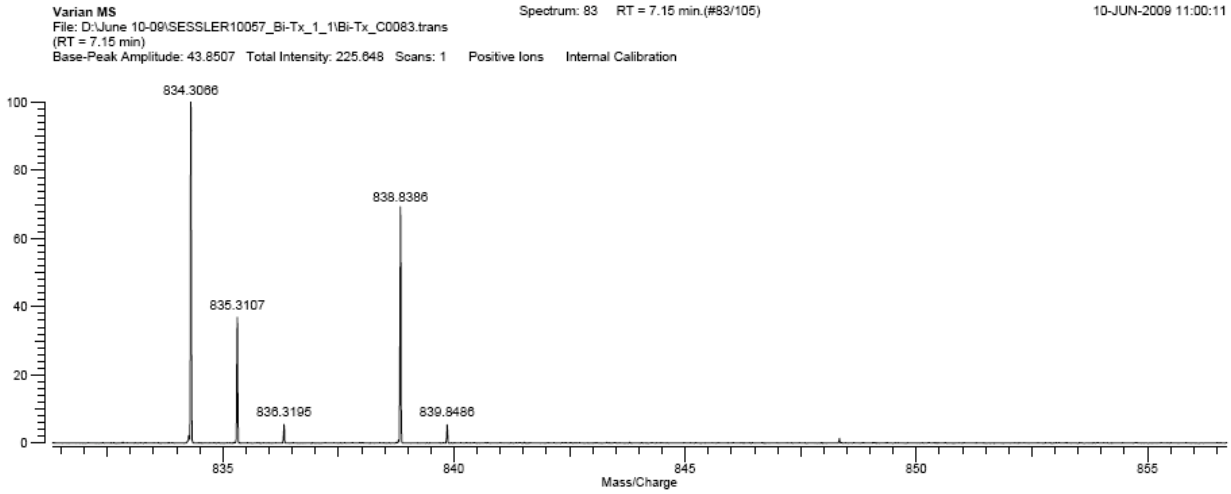
**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C) for **2a**



## **Low Resolution MS** (ESI) for **2a**



**High Resolution MS** (ESI) for **2a**




## Elemental Composition Search Report:

**Target Mass:**

Target m/z = 834.3066 ± 0.002
Charge = +1

**Possible Elements:**

| Element: | Exact Mass: | Min: | Max: |
|---|---|---|---|
| C | 12.000000 | 0 | 100 |
| H | 1.007825 | 0 | 100 |
| N | 14.003074 | 5 | 5 |
| O | 15.994915 | 5 | 5 |
| Bi | 208.980383 | 1 | 1 |

**Additional Search Restrictions:**

None

**Search Results:**

Number of Hits = 1

| m/z | Delta m/z | DBE | Formula |
|---|---|---|---|
| 834.30625 | 0.00035 | 18.0 | $C_{36}H_{43}N_5O_5Bi^{+1}$ |

## 4. Synthesis and Characterization of **2b**

The hydrochloride salt of $sp^3$-$Tex_{OMe}$ (140.6 mg, 216.2 mmol) was dissolved in 20 ml methanol. $Pb(NO_3)_2$ (107.4 mg, 324.3 mmol, 1.5 equiv.) was added together with 1 ml triethylamine. The solution was stirred at 70 °C and gradually changed color from deep red to deep green. The mixture was stirred at that temperature for two hours. The solvent was removed in vacuo and the residue was subjected to column chromatography (silica, first 95% $CH_2Cl_2$ and 5% MeOH, with the product slowly eluting with 60% $CH_2Cl_2$ and 40% MeOH). The deep green fraction was collected and the solvent was removed in vacuo to give **2a** as a deep green crystalline material (123.6 mg, 70%).

**UV/Vis** (MeOH, 25 °C): λ [nm] = 479 (Soret-type band); 740 (Q-type band);

**$^1$H-NMR** (300 MHz, $CD_3OD$, 25 °C): δ[ppm] = 1.62 (t, J = 7.2 Hz, 6 H); 2.19 (t, J = 6.8 Hz, 4 H); 3.66-3.92 (m, 12 H), 4.56 (s, 6 H); 8.58 (s, 2 H); 9.13 (s, 2 H); 11.12 (s, 2 H);

**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C): δ[ppm] = 6.0 (2 C); 17.1 (2 C); 22.7 (2 C); 26.6 (2 C); 32.8 (2 C); 58.3 (2 C); 66.2 (2 C); 97.2 (2 C); 108.3 (2 C); 119.5 (2 C); 120.2 (2 C); 135.5 (2 C); 140.8 (2 C); 148.8 (2 C); 149.9 (2 C); 150.4 (2 C); 159.9 (2 C);

**MS** (ESI): 816.40 ($M^+$, monomeric Pb-Tx, no axial ligand)

**High Resolution MS** (ESI): calculated for $C_{36}H_{42}N_5O_4Pb^{+1}$ = 816.3003; found: 816.29977 ($C_{36}H_{42}N_5O_4Pb^{+1}$, $M^+$)

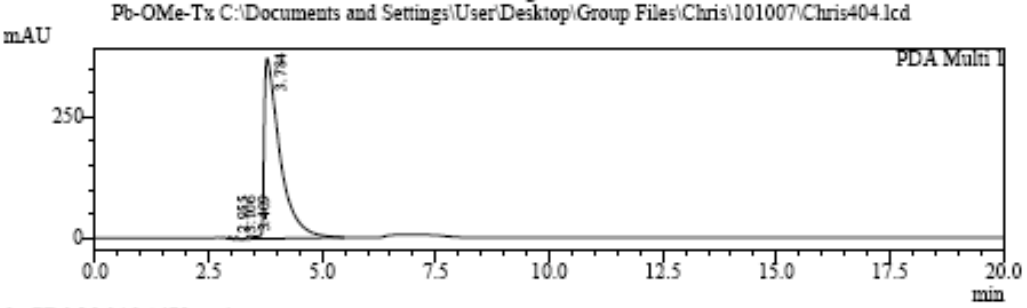
## **HPLC** and **UV/Vis spectrum** for **2b**

Sample Information

Sample Name : Pb-OMe-Tx

Chromatogram

Pb-OMe-Tx C:\Documents and Settings\User\Desktop\Group Files\Chris\101007\Chris404.lcd




1 PDA Multi 1 / 470nm 4nm

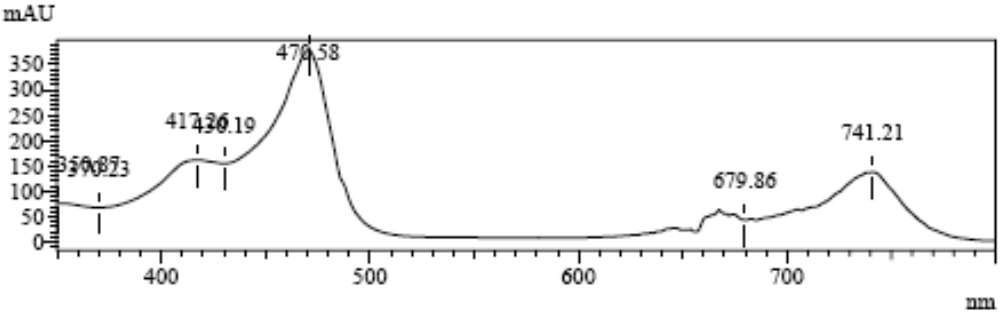
PeakTable

PDA Ch1 470nm 4nm

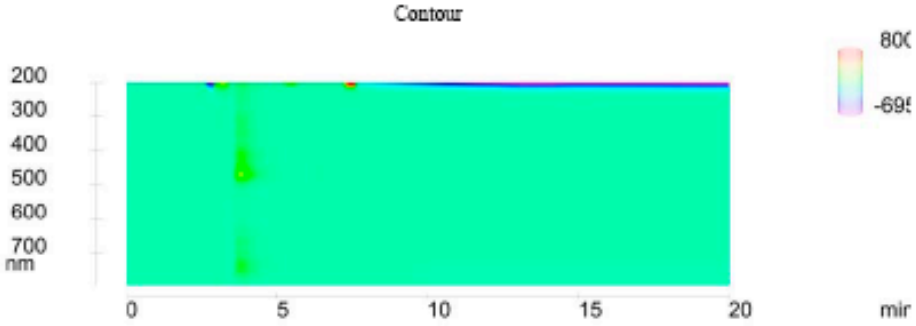
| Peak# | Ret. Time | Area | Area % |
|---|---|---|---|
| 1 | 2.955 | 16754 | 0.184 |
| 2 | 3.106 | 18571 | 0.204 |
| 3 | 3.409 | 72976 | 0.800 |
| 4 | 3.784 | 9015690 | 98.813 |
| Total | | 9123992 | 100.000 |

Spectrum

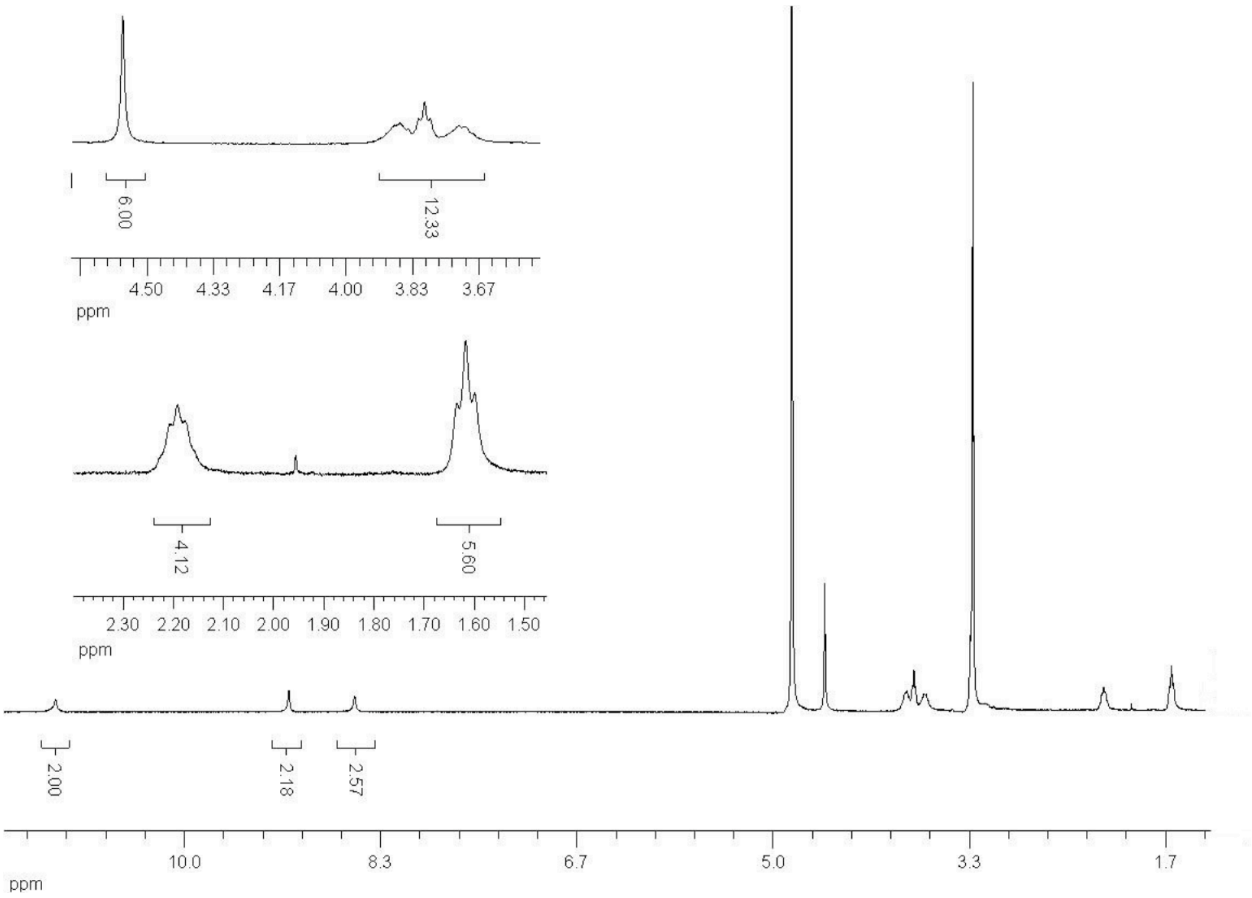
Peak# : 4
Retention Time : 3.784
Compound Name :
Spectrum Operation : None



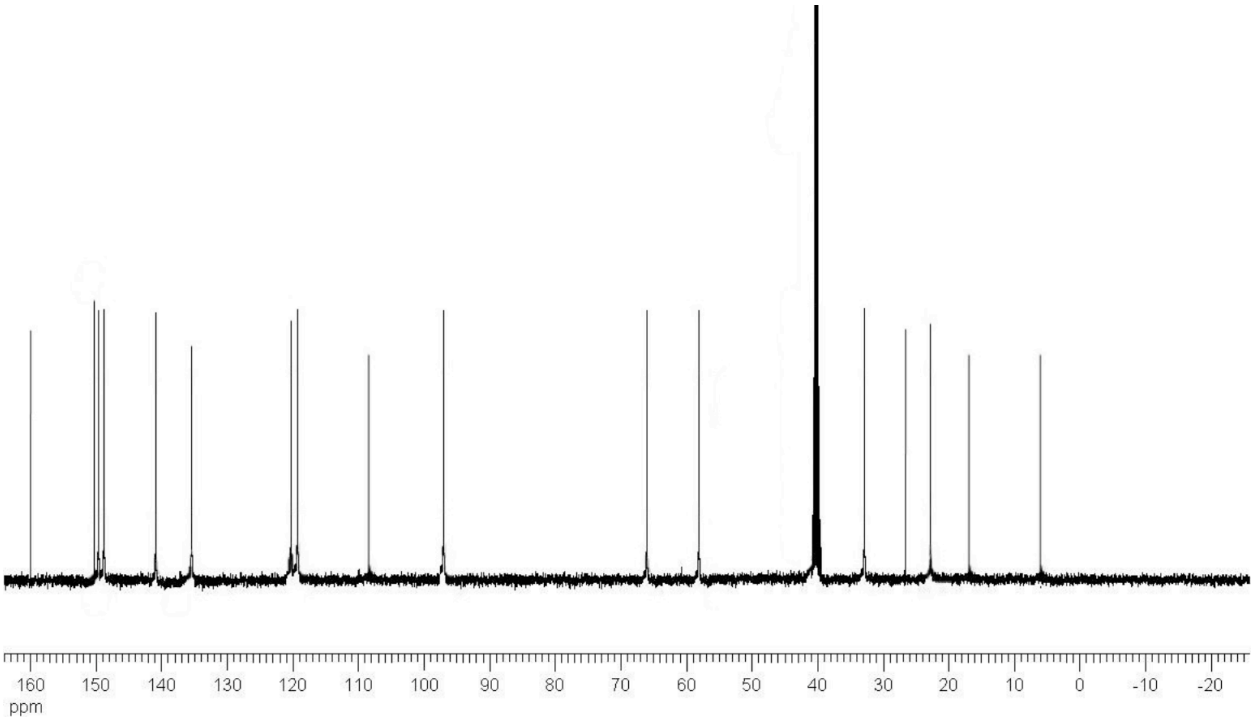

Contour



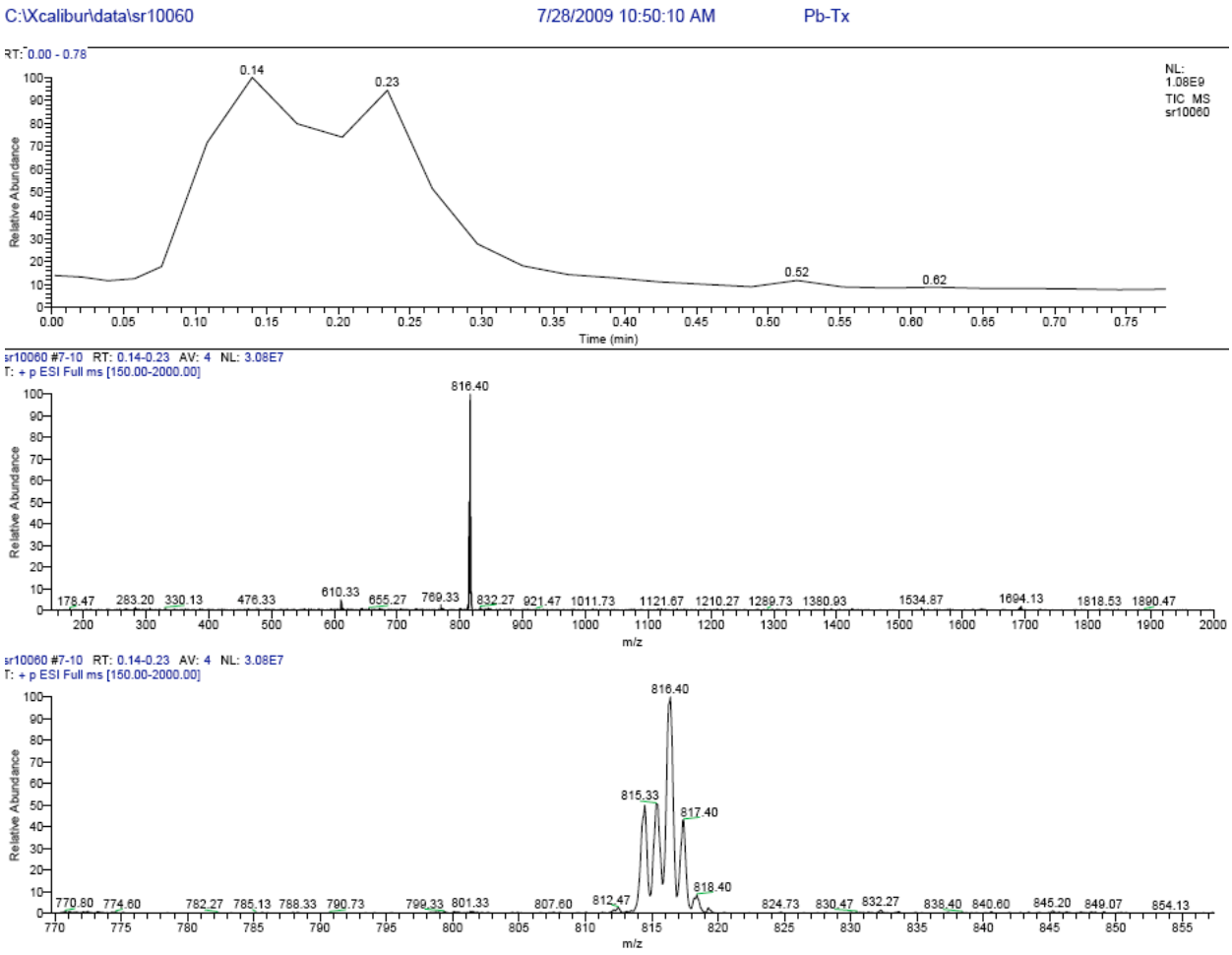
## $^1$**H-NMR** (300 MHz, $CD_3OD$, 25 °C) for **2b**



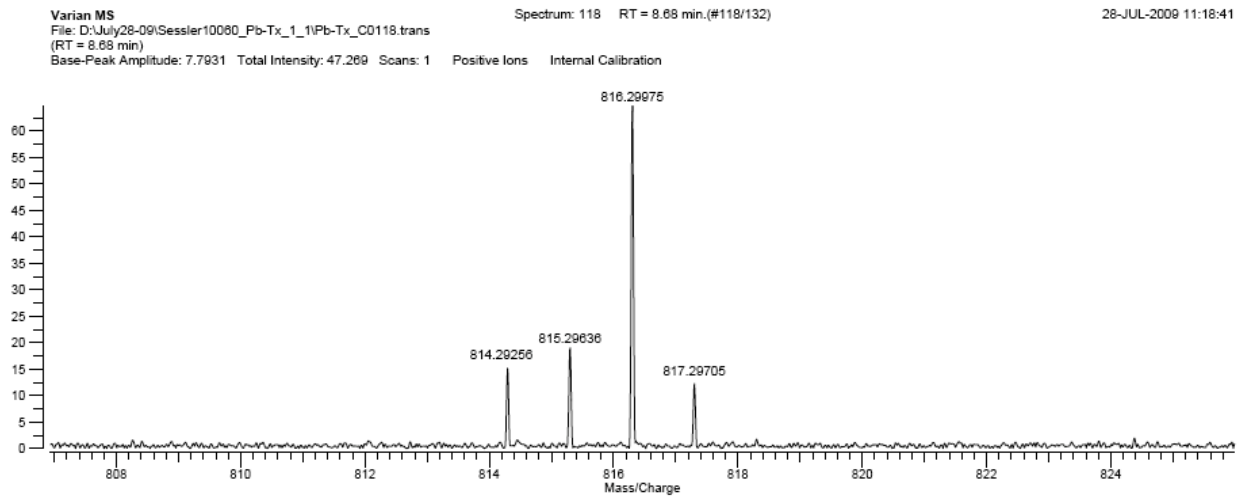
**$^{13}$C-NMR** (125 MHz, DMSO-$d_6$, 25 °C) for **2b**



## **Low Resolution MS** (ESI) for **2b**



**High Resolution MS** (ESI) for **2b**




## Elemental Composition Search Report:

**Target Mass:**

Target m/z = 816.29975 ± .002
Charge = +1

**Possible Elements:**

| Element: | Exact Mass: | Min: | Max: |
|---|---|---|---|
| C | 12.000000 | 0 | 100 |
| H | 1.007825 | 0 | 100 |
| O | 15.994915 | 4 | 5 |
| N | 14.003074 | 5 | 5 |
| Pb | 207.976636 | 1 | 1 |

**Additional Search Restrictions:**

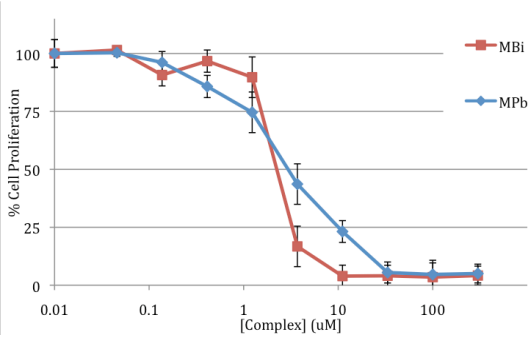
None

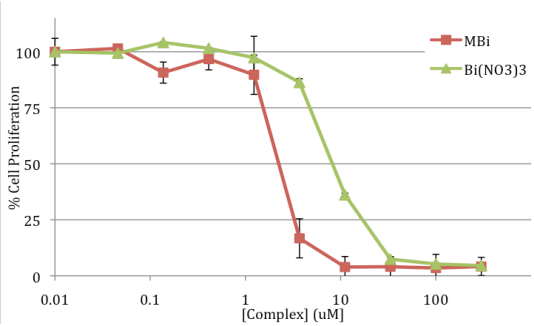
**Search Results:**

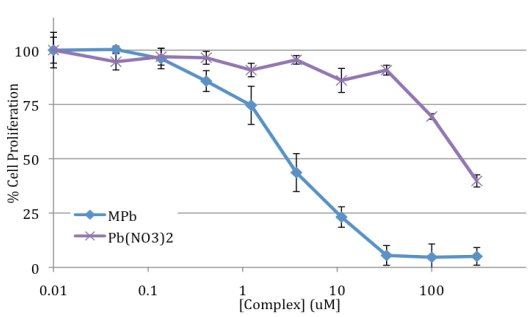
Number of Hits = 1

| m/z | Delta m/z | DBE | Formula |
|---|---|---|---|
| 816.29977 | -0.00002 | 18.5 | $C_{36}H_{42}O_4N_5Pb^{+1}$ |

## 5. *In vitro* anti-proliferative activity of **1a** (MBi) and **1b** (MPb)




The proliferation of exponential phase cultures of A2780 cells was assessed by a dye reduction assay and assessing the formazan product.[5] In brief, tumor cells were seeded in 96-well microtiter plates at 300 cells/well, respectively, and allowed to adhere overnight in RPMI 1640 medium supplemented with 2 mM L-glutamine, 10% heat inactivated fetal bovine serum, and antibiotics (200 U/cm$^3$ penicillin and 200 $\mu$g/cm$^3$ streptomycin). Stock solutions of MBi and MPb (30% v/v methanol/$H_2O$) were formulated in the indicated solvent for maximum stability and then diluted in medium for secondary stocks. Secondary stock solutions were serially diluted in medium and immediately added to wells to give the final concentrations indicated in the figures, whereupon plates were incubated at 37 $^o$C under a 5% $CO_2$/95% air atmosphere. After a total of 5 days, the tetrazolium dye, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT, Sigma Chemical) was added to each well, the plates incubated at 37 $^o$C, whereupon the medium was removed, the formazan dissolved in 50 $\mu$M DMSO and absorbances measured at 560-650 nm using a microplate reader (Molecular Devices, Sunnyvale, CA). Absorbances were corrected for background and the values normalized to wells containing untreated cells to allow plate-to-plate comparison. The data are shown as mean inhibition of proliferation or growth as a % of control cells from 8-10 replicate values. Error bars represent the associated standard deviation.

## 6. Crystallographic Material for **2a** (CCDC-790736)

X-ray Experimental.

Table 1. Crystallographic Data for **2a**.

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for **2a**.

Table 3. Bond Lengths (Å) and Angles ($^o$) for the non-hydrogen atoms of **2a**.

Table 4. Anisotropic displacement parameters.

Table 5. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of **2a**.

Table 6. Torsion Angles ($^o$) for the non-hydrogen atoms of **2a**.

Figure 1. View of the Bi coordination to the macrocycle in **2a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 2. View of the dimer formed in **2a**. Displacement ellipsoids are scaled to the 50% probability level. The oxygen atom bridging the two Bi ions resides on a crystallographic inversion center at ½, ½, 0. The distance between the rings defined by the five nitrogen atoms of the macrocycles is 3.433(5) Å.

## X-ray experimental for $(C_{36}H_{42}N_5O_4)Bi(NO_3)$-$CH_3OH$-$2H_2O$-1/2 O:

Crystals grew as small, dark green prisms by slow evaporation from methanol. The data crystal had approximate dimensions; 0.18 x 0.13 x 0.04 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKa radiation ($\lambda$ = 0.71069 Å). A total of 736 frames of data were collected using w-scans with a scan range of 0.5° and a counting time of 40 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[6] The structure was solved by direct methods using SIR97[7] and refined by full-matrix least-squares on $F^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[8] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(s(F_O))^2 + (0.0789*P)^2 + (0.8963*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.134, with R(F) equal to 0.0479 and a goodness of fit, S = 1.094. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[9] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[10] All figures were generated using SHELXTL/PC.[11] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 1 Crystallographic data for **2a**.

| | | |
|---|---|---|
| Empirical formula | C74 H100 Bi2 N12 O21 | |
| Formula weight | 1911.62 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71069 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.9258(8) Å | α= 75.646(3)°. |
| | b = 12.9230(10) Å | β= 74.471(3)°. |
| | c = 15.3223(15) Å | γ = 88.263(2)°. |
| Volume | 2017.9(3) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 1.573 $Mg/m^3$ | |
| Absorption coefficient | 4.432 $mm^{-1}$ | |
| F(000) | 962 | |
| Crystal size | 0.18 x 0.13 x 0.04 mm | |
| Theta range for data collection | 3.08 to 27.48°. | |
| Index ranges | -14<=h<=12, -10<=k<=16, -19<=l<=19 | |
| Reflections collected | 16942 | |
| Independent reflections | 9198 [R(int) = 0.0405] | |
| Completeness to theta = 27.48° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.84 and 0.66 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9198 / 41 / 479 | |
| Goodness-of-fit on $F^2$ | 1.094 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0479, wR2 = 0.1288 | |
| R indices (all data) | R1 = 0.0557, wR2 = 0.1341 | |
| Largest diff. peak and hole | 1.893 and -2.670 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Bi1 | 5961(1) | 5952(1) | 642(1) | 33(1) |
| O1W | 5000 | 5000 | 0 | 47(2) |
| O1A | 5872(6) | 7117(7) | 1955(5) | 112(3) |
| C2A | 5195(8) | 7201(8) | 2860(6) | 72(2) |
| O1B | 8522(5) | 6881(6) | 461(4) | 82(2) |
| O2B | 9885(5) | 7369(5) | 1043(4) | 62(1) |
| N1B | 8863(6) | 7445(6) | 901(4) | 55(2) |
| O3B | 8127(7) | 8128(6) | 1252(6) | 95(2) |
| O1 | 10408(5) | 7402(4) | -3842(3) | 52(1) |
| O2 | 11378(4) | 5692(4) | -3116(3) | 43(1) |
| O4 | 918(10) | 9850(8) | 2178(6) | 127(3) |
| N1 | 3984(5) | 5481(4) | 1884(3) | 34(1) |
| N2 | 4563(5) | 7207(4) | 94(3) | 37(1) |
| N3 | 6771(5) | 6867(4) | -1076(3) | 38(1) |
| N4 | 7803(4) | 5094(4) | -308(3) | 34(1) |
| N5 | 6274(4) | 4180(4) | 1419(3) | 33(1) |
| C1 | 3779(5) | 4645(5) | 2677(4) | 34(1) |
| C2 | 2587(5) | 4763(5) | 3345(4) | 38(1) |
| C3 | 2091(6) | 5679(5) | 2959(4) | 40(1) |
| C4 | 2959(5) | 6120(5) | 2051(4) | 35(1) |
| C5 | 2760(6) | 7093(5) | 1455(4) | 39(1) |
| C6 | 3471(6) | 7595(5) | 568(5) | 40(1) |
| C7 | 3221(6) | 8616(5) | -22(5) | 42(1) |
| C8 | 4175(6) | 8808(5) | -841(5) | 42(1) |
| C9 | 4993(6) | 7908(5) | -743(5) | 41(1) |
| C10 | 6150(6) | 7708(5) | -1371(4) | 40(1) |
| C11 | 7927(6) | 6590(5) | -1602(4) | 36(1) |
| C12 | 8561(6) | 7208(5) | -2505(4) | 40(1) |
| C13 | 9705(6) | 6881(5) | -2982(4) | 41(1) |
| C14 | 10251(6) | 5933(5) | -2571(4) | 38(1) |
| C15 | 9651(5) | 5338(5) | -1690(4) | 36(1) |

| | | | | |
|---|---|---|---|---|
| C16 | 8462(5) | 5646(5) | -1181(4) | 33(1) |
| C17 | 8147(5) | 4170(5) | 163(4) | 36(1) |
| C18 | 7360(5) | 3705(5) | 1070(4) | 35(1) |
| C19 | 7523(6) | 2731(5) | 1726(4) | 39(1) |
| C20 | 6462(6) | 2624(5) | 2485(4) | 40(1) |
| C21 | 5709(5) | 3532(5) | 2279(4) | 36(1) |
| C22 | 4548(5) | 3765(5) | 2847(4) | 34(1) |
| C23 | 2068(6) | 4026(6) | 4283(4) | 47(2) |
| C24 | 2622(8) | 4253(7) | 5044(5) | 59(2) |
| C25 | 876(6) | 6181(6) | 3357(5) | 47(2) |
| C26 | 1110(8) | 7045(6) | 3821(5) | 56(2) |
| C27 | 2155(6) | 9313(5) | 253(6) | 49(2) |
| C28 | 2507(7) | 10142(6) | 731(6) | 54(2) |
| C29 | 1361(9) | 10564(7) | 1308(6) | 69(2) |
| C30 | 4341(8) | 9748(6) | -1650(6) | 62(2) |
| C31 | 9996(8) | 8432(6) | -4256(5) | 60(2) |
| C32 | 12020(6) | 4810(6) | -2721(4) | 47(2) |
| C33 | 8622(6) | 2012(5) | 1563(5) | 45(2) |
| C34 | 6168(8) | 1756(6) | 3401(5) | 64(2) |
| C35 | 6341(11) | 2127(8) | 4249(6) | 105(3) |
| C36 | 5942(13) | 1291(9) | 5146(6) | 166(5) |
| O3 | 6932(13) | 537(9) | 5249(6) | 270(8) |

Table 3. Bond lengths [Å] and angles [°] for **2a**.

| | | | |
|---|---|---|---|
| Bi1-O1W | 2.1941(2) | C2-C23 | 1.487(9) |
| Bi1-N2 | 2.352(5) | C3-C4 | 1.447(8) |
| Bi1-N5 | 2.366(5) | C3-C25 | 1.505(8) |
| Bi1-N1 | 2.442(5) | C4-C5 | 1.407(9) |
| Bi1-N3 | 2.527(5) | C5-C6 | 1.379(9) |
| Bi1-N4 | 2.548(4) | C5-H5 | 0.95 |
| O1W-Bi1#1 | 2.1941(2) | C6-C7 | 1.467(9) |
| O1A-C2A | 1.415(9) | C7-C8 | 1.372(10) |
| O1A-H1A | 0.8400 | C7-C27 | 1.486(8) |
| C2A-H2A1 | 0.98 | C8-C9 | 1.449(8) |
| C2A-H2A2 | 0.98 | C8-C30 | 1.481(10) |
| C2A-H2A3 | 0.98 | C9-C10 | 1.430(8) |
| O1B-N1B | 1.232(9) | C10-H10 | 0.95 |
| O2B-N1B | 1.190(8) | C11-C16 | 1.420(8) |
| N1B-O3B | 1.294(9) | C11-C12 | 1.416(9) |
| O1-C13 | 1.353(8) | C12-C13 | 1.381(8) |
| O1-C31 | 1.440(9) | C12-H12 | 0.95 |
| O2-C14 | 1.366(7) | C13-C14 | 1.423(9) |
| O2-C32 | 1.412(8) | C14-C15 | 1.373(9) |
| O4-C29 | 1.391(12) | C15-C16 | 1.426(7) |
| O4-H4 | 0.8400 | C15-H15 | 0.95 |
| N1-C4 | 1.377(7) | C17-C18 | 1.418(8) |
| N1-C1 | 1.382(8) | C17-H17 | 0.95 |
| N2-C9 | 1.346(8) | C18-C19 | 1.442(8) |
| N2-C6 | 1.372(7) | C19-C20 | 1.387(9) |
| N3-C10 | 1.312(8) | C19-C33 | 1.502(8) |
| N3-C11 | 1.394(7) | C20-C21 | 1.433(8) |
| N4-C17 | 1.334(8) | C20-C34 | 1.526(9) |
| N4-C16 | 1.362(7) | C21-C22 | 1.404(7) |
| N5-C18 | 1.361(6) | C22-H22 | 0.95 |
| N5-C21 | 1.366(8) | C23-C24 | 1.539(9) |
| C1-C22 | 1.407(8) | C23-H23A | 0.99 |
| C1-C2 | 1.456(7) | C23-H23B | 0.99 |
| C2-C3 | 1.353(9) | C24-H24A | 0.98 |

| | | | |
|---|---|---|---|
| C24-H24B | 0.98 | C31-H31A | 0.98 |
| C24-H24C | 0.98 | C31-H31B | 0.98 |
| C25-C26 | 1.525(9) | C31-H31C | 0.98 |
| C25-H25A | 0.99 | C32-H32A | 0.98 |
| C25-H25B | 0.99 | C32-H32B | 0.98 |
| C26-H26A | 0.98 | C32-H32C | 0.98 |
| C26-H26B | 0.98 | C33-H33A | 0.98 |
| C26-H26C | 0.98 | C33-H33B | 0.98 |
| C27-C28 | 1.548(9) | C33-H33C | 0.98 |
| C27-H27A | 0.99 | C34-C35 | 1.549(9) |
| C27-H27B | 0.99 | C34-H34A | 0.99 |
| C28-C29 | 1.500(9) | C34-H34B | 0.99 |
| C28-H28A | 0.99 | C35-C36 | 1.489(8) |
| C28-H28B | 0.99 | C35-H35A | 0.99 |
| C29-H29A | 0.99 | C35-H35B | 0.99 |
| C29-H29B | 0.99 | C36-O3 | 1.4484 |
| C30-H30A | 0.98 | C36-H36A | 0.99 |
| C30-H30B | 0.98 | C36-H36B | 0.99 |
| C30-H30C | 0.98 | O3-H3 | 0.84 |

| | |
|---|---|
| O1W-Bi1-N2 | 79.53(12) |
| O1W-Bi1-N5 | 77.57(11) |
| N2-Bi1-N5 | 148.07(18) |
| O1W-Bi1-N1 | 80.93(10) |
| N2-Bi1-N1 | 77.58(17) |
| N5-Bi1-N1 | 77.09(16) |
| O1W-Bi1-N3 | 77.96(11) |
| N2-Bi1-N3 | 66.83(16) |
| N5-Bi1-N3 | 128.30(15) |
| N1-Bi1-N3 | 141.18(16) |
| O1W-Bi1-N4 | 77.22(11) |
| N2-Bi1-N4 | 128.26(16) |
| N5-Bi1-N4 | 67.08(16) |
| N1-Bi1-N4 | 141.13(16) |
| N3-Bi1-N4 | 63.44(15) |
| Bi1#1-O1W-Bi1 | 180.000(8) |
| C2A-O1A-H1A | 110.0 |
| O1A-C2A-H2A1 | 109.5 |
| O1A-C2A-H2A2 | 109.5 |
| H2A1-C2A-H2A2 | 109.5 |
| O1A-C2A-H2A3 | 109.5 |
| H2A1-C2A-H2A3 | 109.5 |
| H2A2-C2A-H2A3 | 109.5 |
| O2B-N1B-O1B | 121.2(7) |
| O2B-N1B-O3B | 116.4(8) |
| O1B-N1B-O3B | 122.3(7) |
| C13-O1-C31 | 117.4(5) |
| C14-O2-C32 | 117.7(5) |
| C29-O4-H4 | 110.0 |
| C4-N1-C1 | 105.2(5) |
| C4-N1-Bi1 | 126.5(4) |
| C1-N1-Bi1 | 126.7(4) |
| C9-N2-C6 | 107.6(5) |
| C9-N2-Bi1 | 118.7(4) |
| C6-N2-Bi1 | 130.7(4) |
| C10-N3-C11 | 123.7(6) |

| | |
|---|---|
| C10-N3-Bi1 | 115.2(4) |
| C11-N3-Bi1 | 120.1(4) |
| C17-N4-C16 | 124.7(5) |
| C17-N4-Bi1 | 114.7(4) |
| C16-N4-Bi1 | 120.0(4) |
| C18-N5-C21 | 106.4(5) |
| C18-N5-Bi1 | 118.6(4) |
| C21-N5-Bi1 | 133.8(4) |
| N1-C1-C22 | 127.5(5) |
| N1-C1-C2 | 110.3(5) |
| C22-C1-C2 | 122.2(6) |
| C3-C2-C1 | 106.7(5) |
| C3-C2-C23 | 127.8(5) |
| C1-C2-C23 | 125.4(6) |
| C2-C3-C4 | 106.9(5) |
| C2-C3-C25 | 128.7(6) |
| C4-C3-C25 | 124.4(6) |
| N1-C4-C5 | 126.5(5) |
| N1-C4-C3 | 110.8(5) |
| C5-C4-C3 | 122.7(5) |
| C6-C5-C4 | 129.4(5) |
| C6-C5-H5 | 115.3 |
| C4-C5-H5 | 115.3 |
| N2-C6-C5 | 124.3(6) |
| N2-C6-C7 | 108.5(6) |
| C5-C6-C7 | 127.1(5) |
| C8-C7-C6 | 107.1(5) |
| C8-C7-C27 | 127.6(6) |
| C6-C7-C27 | 125.3(6) |
| C7-C8-C9 | 105.7(6) |
| C7-C8-C30 | 127.1(6) |
| C9-C8-C30 | 127.3(6) |
| N2-C9-C10 | 119.2(5) |
| N2-C9-C8 | 111.1(6) |
| C10-C9-C8 | 129.7(6) |
| N3-C10-C9 | 117.4(6) |

| | |
|---|---|
| N3-C10-H10 | 121.3 |
| C9-C10-H10 | 121.3 |
| N3-C11-C16 | 116.4(5) |
| N3-C11-C12 | 122.9(5) |
| C16-C11-C12 | 120.6(5) |
| C13-C12-C11 | 119.5(6) |
| C13-C12-H12 | 120.3 |
| C11-C12-H12 | 120.3 |
| O1-C13-C12 | 125.2(6) |
| O1-C13-C14 | 114.2(5) |
| C12-C13-C14 | 120.6(6) |
| C15-C14-O2 | 124.8(6) |
| C15-C14-C13 | 120.3(5) |
| O2-C14-C13 | 114.9(5) |
| C14-C15-C16 | 120.7(6) |
| C14-C15-H15 | 119.7 |
| C16-C15-H15 | 119.7 |
| N4-C16-C11 | 117.4(5) |
| N4-C16-C15 | 124.2(5) |
| C11-C16-C15 | 118.3(5) |
| N4-C17-C18 | 117.6(5) |
| N4-C17-H17 | 121.2 |
| C18-C17-H17 | 121.2 |
| N5-C18-C17 | 120.1(5) |
| N5-C18-C19 | 111.1(5) |
| C17-C18-C19 | 128.8(5) |
| C20-C19-C18 | 105.3(5) |
| C20-C19-C33 | 129.8(6) |
| C18-C19-C33 | 124.9(6) |
| C19-C20-C21 | 106.9(5) |
| C19-C20-C34 | 127.7(6) |
| C21-C20-C34 | 125.3(6) |
| N5-C21-C22 | 122.5(5) |
| N5-C21-C20 | 110.4(5) |
| C22-C21-C20 | 127.2(6) |
| C21-C22-C1 | 129.2(6) |

| | |
|---|---|
| C21-C22-H22 | 115.4 |
| C1-C22-H22 | 115.4 |
| C2-C23-C24 | 113.6(6) |
| C2-C23-H23A | 108.8 |
| C24-C23-H23A | 108.8 |
| C2-C23-H23B | 108.8 |
| C24-C23-H23B | 108.8 |
| H23A-C23-H23B | 107.7 |
| C23-C24-H24A | 109.5 |
| C23-C24-H24B | 109.5 |
| H24A-C24-H24B | 109.5 |
| C23-C24-H24C | 109.5 |
| H24A-C24-H24C | 109.5 |
| H24B-C24-H24C | 109.5 |
| C3-C25-C26 | 111.7(5) |
| C3-C25-H25A | 109.3 |
| C26-C25-H25A | 109.3 |
| C3-C25-H25B | 109.3 |
| C26-C25-H25B | 109.3 |
| H25A-C25-H25B | 107.9 |
| C25-C26-H26A | 109.5 |
| C25-C26-H26B | 109.5 |
| H26A-C26-H26B | 109.5 |
| C25-C26-H26C | 109.5 |
| H26A-C26-H26C | 109.5 |
| H26B-C26-H26C | 109.5 |
| C7-C27-C28 | 112.7(5) |
| C7-C27-H27A | 109.0 |
| C28-C27-H27A | 109.0 |
| C7-C27-H27B | 109.0 |
| C28-C27-H27B | 109.0 |
| H27A-C27-H27B | 107.8 |
| C29-C28-C27 | 112.6(7) |
| C29-C28-H28A | 109.1 |
| C27-C28-H28A | 109.1 |
| C29-C28-H28B | 109.1 |

| | |
|---|---|
| C27-C28-H28B | 109.1 |
| H28A-C28-H28B | 107.8 |
| O4-C29-C28 | 110.4(8) |
| O4-C29-H29A | 109.6 |
| C28-C29-H29A | 109.6 |
| O4-C29-H29B | 109.6 |
| C28-C29-H29B | 109.6 |
| H29A-C29-H29B | 108.1 |
| C8-C30-H30A | 109.5 |
| C8-C30-H30B | 109.5 |
| H30A-C30-H30B | 109.5 |
| C8-C30-H30C | 109.5 |
| H30A-C30-H30C | 109.5 |
| H30B-C30-H30C | 109.5 |
| O1-C31-H31A | 109.5 |
| O1-C31-H31B | 109.5 |
| H31A-C31-H31B | 109.5 |
| O1-C31-H31C | 109.5 |
| H31A-C31-H31C | 109.5 |
| H31B-C31-H31C | 109.5 |
| O2-C32-H32A | 109.5 |
| O2-C32-H32B | 109.5 |
| H32A-C32-H32B | 109.5 |
| O2-C32-H32C | 109.5 |
| H32A-C32-H32C | 109.5 |
| H32B-C32-H32C | 109.5 |
| C19-C33-H33A | 109.5 |
| C19-C33-H33B | 109.5 |
| H33A-C33-H33B | 109.5 |
| C19-C33-H33C | 109.5 |
| H33A-C33-H33C | 109.5 |
| H33B-C33-H33C | 109.5 |
| C20-C34-C35 | 114.4(7) |
| C20-C34-H34A | 108.7 |
| C35-C34-H34A | 108.6 |
| C20-C34-H34B | 108.7 |

| | |
|---|---|
| C35-C34-H34B | 108.7 |
| H34A-C34-H34B | 107.6 |
| C36-C35-C34 | 113.1(7) |
| C36-C35-H35A | 109.0 |
| C34-C35-H35A | 109.0 |
| C36-C35-H35B | 109.0 |
| C34-C35-H35B | 109.0 |
| H35A-C35-H35B | 107.8 |
| O3-C36-C35 | 111.2(6) |
| O3-C36-H36A | 109.4 |
| C35-C36-H36A | 109.4 |
| O3-C36-H36B | 109.4 |
| C35-C36-H36B | 109.4 |
| H36A-C36-H36B | 108.0 |
| C36-O3-H3 | 109.5 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Bi1 | 32(1) | 39(1) | 37(1) | -19(1) | -14(1) | 11(1) |
| O1W | 34(3) | 68(4) | 52(4) | -41(3) | -12(3) | -5(3) |
| O1A | 71(4) | 167(8) | 111(5) | -110(6) | 29(4) | -37(5) |
| C2A | 57(5) | 103(7) | 70(5) | -57(5) | -10(4) | 1(5) |
| O1B | 47(3) | 143(6) | 58(3) | -32(4) | -7(3) | -30(4) |
| O2B | 46(3) | 62(3) | 83(4) | -33(3) | -14(3) | 6(3) |
| N1B | 38(3) | 69(4) | 49(3) | -13(3) | 0(3) | 16(3) |
| O3B | 61(4) | 78(4) | 144(7) | -33(5) | -20(4) | 32(3) |
| O1 | 51(3) | 55(3) | 41(2) | -14(2) | 1(2) | 2(2) |
| O2 | 34(2) | 55(3) | 40(2) | -22(2) | 0(2) | 3(2) |
| O4 | 132(8) | 127(8) | 94(6) | -17(5) | 5(6) | 26(6) |
| N1 | 33(2) | 38(2) | 40(2) | -23(2) | -14(2) | 12(2) |
| N2 | 38(3) | 40(3) | 40(2) | -21(2) | -13(2) | 18(2) |
| N3 | 37(3) | 45(3) | 41(3) | -24(2) | -18(2) | 16(2) |
| N4 | 25(2) | 46(3) | 35(2) | -18(2) | -8(2) | 12(2) |
| N5 | 25(2) | 43(3) | 33(2) | -17(2) | -8(2) | 13(2) |
| C1 | 30(3) | 46(3) | 35(3) | -25(2) | -9(2) | 8(2) |
| C2 | 24(3) | 58(4) | 38(3) | -27(3) | -5(2) | 4(3) |
| C3 | 29(3) | 54(4) | 45(3) | -31(3) | -6(2) | 8(3) |
| C4 | 26(3) | 46(3) | 41(3) | -27(3) | -9(2) | 10(2) |
| C5 | 30(3) | 51(3) | 48(3) | -32(3) | -14(2) | 17(3) |
| C6 | 35(3) | 46(3) | 53(3) | -32(3) | -22(3) | 20(3) |
| C7 | 39(3) | 37(3) | 62(4) | -23(3) | -25(3) | 19(3) |
| C8 | 36(3) | 38(3) | 60(4) | -18(3) | -23(3) | 14(3) |
| C9 | 39(3) | 42(3) | 50(3) | -20(3) | -20(3) | 16(3) |
| C10 | 43(3) | 43(3) | 39(3) | -17(3) | -13(3) | 13(3) |
| C11 | 34(3) | 41(3) | 41(3) | -22(3) | -13(2) | 12(2) |
| C12 | 40(3) | 41(3) | 42(3) | -17(3) | -12(3) | 5(3) |
| C13 | 43(3) | 44(3) | 38(3) | -19(3) | -7(3) | 0(3) |
| C14 | 28(3) | 50(3) | 40(3) | -23(3) | -6(2) | 4(2) |
| C15 | 25(3) | 47(3) | 42(3) | -23(3) | -9(2) | 8(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 26(3) | 42(3) | 32(3) | -16(2) | -6(2) | 4(2) |
| C17 | 28(3) | 45(3) | 43(3) | -23(3) | -10(2) | 14(2) |
| C18 | 28(3) | 39(3) | 42(3) | -18(2) | -10(2) | 15(2) |
| C19 | 36(3) | 41(3) | 44(3) | -16(3) | -16(3) | 15(3) |
| C20 | 35(3) | 42(3) | 46(3) | -15(3) | -11(3) | 13(3) |
| C21 | 30(3) | 45(3) | 38(3) | -18(3) | -13(2) | 9(2) |
| C22 | 27(3) | 49(3) | 30(2) | -18(2) | -7(2) | 7(2) |
| C23 | 35(3) | 64(4) | 42(3) | -24(3) | -3(3) | 6(3) |
| C24 | 60(5) | 80(5) | 41(3) | -29(4) | -8(3) | 10(4) |
| C25 | 33(3) | 63(4) | 50(3) | -31(3) | -5(3) | 12(3) |
| C26 | 58(4) | 58(4) | 59(4) | -36(4) | -8(3) | 22(4) |
| C27 | 34(3) | 45(3) | 77(5) | -24(3) | -25(3) | 18(3) |
| C28 | 42(4) | 52(4) | 79(5) | -38(4) | -17(3) | 17(3) |
| C29 | 63(5) | 69(5) | 70(5) | -32(4) | 0(4) | 26(4) |
| C30 | 53(4) | 41(4) | 86(6) | -4(4) | -18(4) | 14(3) |
| C31 | 68(5) | 54(4) | 49(4) | -10(3) | -2(4) | 0(4) |
| C32 | 33(3) | 72(4) | 42(3) | -30(3) | -4(3) | 8(3) |
| C33 | 37(3) | 47(3) | 54(4) | -18(3) | -12(3) | 21(3) |
| C34 | 51(4) | 62(4) | 61(4) | 4(4) | -4(3) | 16(4) |
| C35 | 89(5) | 116(6) | 92(5) | 23(4) | -39(4) | 0(5) |
| C36 | 151(7) | 161(7) | 169(7) | -8(6) | -47(6) | 13(6) |
| O3 | 256(10) | 261(11) | 280(10) | -42(8) | -72(8) | 18(8) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for **2a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H1A | 6569 | 7464 | 1783 | 168 |
| H2A1 | 5796 | 7339 | 3196 | 107 |
| H2A2 | 4709 | 6531 | 3204 | 107 |
| H2A3 | 4612 | 7790 | 2808 | 107 |
| H4 | 328 | 9453 | 2171 | 190 |
| H5 | 2030 | 7456 | 1701 | 47 |
| H10 | 6458 | 8166 | -1979 | 48 |
| H12 | 8202 | 7842 | -2782 | 47 |
| H15 | 10033 | 4716 | -1416 | 43 |
| H17 | 8894 | 3836 | -100 | 44 |
| H22 | 4238 | 3256 | 3429 | 41 |
| H23A | 2248 | 3282 | 4239 | 56 |
| H23B | 1134 | 4083 | 4474 | 56 |
| H24A | 3546 | 4189 | 4865 | 89 |
| H24B | 2251 | 3737 | 5640 | 89 |
| H24C | 2420 | 4979 | 5110 | 89 |
| H25A | 281 | 5621 | 3823 | 56 |
| H25B | 474 | 6499 | 2849 | 56 |
| H26A | 1630 | 6763 | 4253 | 84 |
| H26B | 295 | 7261 | 4169 | 84 |
| H26C | 1557 | 7665 | 3341 | 84 |
| H27A | 1418 | 8861 | 687 | 59 |
| H27B | 1897 | 9695 | -311 | 59 |
| H28A | 3052 | 9806 | 1137 | 65 |
| H28B | 3004 | 10746 | 245 | 65 |
| H29A | 1585 | 11263 | 1391 | 83 |
| H29B | 683 | 10672 | 979 | 83 |
| H30A | 3507 | 10023 | -1692 | 93 |
| H30B | 4768 | 9538 | -2226 | 93 |
| H30C | 4857 | 10307 | -1569 | 93 |

| | | | | |
|---|---|---|---|---|
| H31A | 9170 | 8346 | -4372 | 91 |
| H31B | 10621 | 8752 | -4849 | 91 |
| H31C | 9917 | 8898 | -3829 | 91 |
| H32A | 12104 | 4879 | -2117 | 71 |
| H32B | 12867 | 4791 | -3143 | 71 |
| H32C | 11535 | 4148 | -2630 | 71 |
| H33A | 9422 | 2428 | 1403 | 68 |
| H33B | 8602 | 1696 | 1047 | 68 |
| H33C | 8561 | 1441 | 2132 | 68 |
| H34A | 6728 | 1152 | 3313 | 77 |
| H34B | 5279 | 1487 | 3546 | 77 |
| H35A | 7247 | 2334 | 4132 | 126 |
| H35B | 5839 | 2769 | 4308 | 126 |
| H36A | 5740 | 1636 | 5675 | 199 |
| H36B | 5163 | 906 | 5164 | 199 |
| H3 | 6773 | -15 | 5096 | 406 |

Table 6. Torsion angles [°] for **2a**

| | |
|---|---|
| O1W-Bi1-N1-C4 | -100.0(4) |
| N2-Bi1-N1-C4 | -18.8(4) |
| N5-Bi1-N1-C4 | -179.2(4) |
| N3-Bi1-N1-C4 | -42.3(5) |
| N4-Bi1-N1-C4 | -156.3(4) |
| O1W-Bi1-N1-C1 | 96.3(4) |
| N2-Bi1-N1-C1 | 177.5(4) |
| N5-Bi1-N1-C1 | 17.0(4) |
| N3-Bi1-N1-C1 | 153.9(4) |
| N4-Bi1-N1-C1 | 40.0(5) |
| O1W-Bi1-N2-C9 | -95.5(4) |
| N5-Bi1-N2-C9 | -140.2(4) |
| N1-Bi1-N2-C9 | -178.4(4) |
| N3-Bi1-N2-C9 | -14.2(4) |
| N4-Bi1-N2-C9 | -31.1(5) |
| O1W-Bi1-N2-C6 | 106.6(5) |
| N5-Bi1-N2-C6 | 61.8(6) |
| N1-Bi1-N2-C6 | 23.6(5) |
| N3-Bi1-N2-C6 | -172.2(6) |
| N4-Bi1-N2-C6 | 171.0(5) |
| O1W-Bi1-N3-C10 | 96.0(4) |
| N2-Bi1-N3-C10 | 12.3(4) |
| N5-Bi1-N3-C10 | 159.3(4) |
| N1-Bi1-N3-C10 | 37.5(5) |
| N4-Bi1-N3-C10 | 177.6(5) |
| O1W-Bi1-N3-C11 | -94.9(4) |
| N2-Bi1-N3-C11 | -178.6(5) |
| N5-Bi1-N3-C11 | -31.6(5) |
| N1-Bi1-N3-C11 | -153.5(4) |
| N4-Bi1-N3-C11 | -13.3(4) |
| O1W-Bi1-N4-C17 | -92.5(4) |
| N2-Bi1-N4-C17 | -157.9(4) |
| N5-Bi1-N4-C17 | -10.8(4) |
| N1-Bi1-N4-C17 | -35.1(5) |

| | |
|---|---|
| N3-Bi1-N4-C17 | -175.3(5) |
| O1W-Bi1-N4-C16 | 96.3(4) |
| N2-Bi1-N4-C16 | 30.9(5) |
| N5-Bi1-N4-C16 | 178.0(4) |
| N1-Bi1-N4-C16 | 153.7(4) |
| N3-Bi1-N4-C16 | 13.5(4) |
| O1W-Bi1-N5-C18 | 93.3(4) |
| N2-Bi1-N5-C18 | 138.4(4) |
| N1-Bi1-N5-C18 | 176.7(4) |
| N3-Bi1-N5-C18 | 29.8(5) |
| N4-Bi1-N5-C18 | 12.1(4) |
| O1W-Bi1-N5-C21 | -101.6(5) |
| N2-Bi1-N5-C21 | -56.4(6) |
| N1-Bi1-N5-C21 | -18.2(5) |
| N3-Bi1-N5-C21 | -165.1(5) |
| N4-Bi1-N5-C21 | 177.2(6) |
| C4-N1-C1-C22 | 178.9(5) |
| Bi1-N1-C1-C22 | -14.6(8) |
| C4-N1-C1-C2 | 0.8(6) |
| Bi1-N1-C1-C2 | 167.4(3) |
| N1-C1-C2-C3 | -1.1(6) |
| C22-C1-C2-C3 | -179.3(5) |
| N1-C1-C2-C23 | -178.8(5) |
| C22-C1-C2-C23 | 3.1(9) |
| C1-C2-C3-C4 | 0.9(6) |
| C23-C2-C3-C4 | 178.4(6) |
| C1-C2-C3-C25 | -179.5(6) |
| C23-C2-C3-C25 | -1.9(10) |
| C1-N1-C4-C5 | 177.8(5) |
| Bi1-N1-C4-C5 | 11.2(8) |
| C1-N1-C4-C3 | -0.3(6) |
| Bi1-N1-C4-C3 | -166.9(4) |
| C2-C3-C4-N1 | -0.4(6) |
| C25-C3-C4-N1 | 180.0(5) |
| C2-C3-C4-C5 | -178.6(5) |
| C25-C3-C4-C5 | 1.8(9) |

| | |
|---|---|
| N1-C4-C5-C6 | 4.4(10) |
| C3-C4-C5-C6 | -177.7(6) |
| C9-N2-C6-C5 | -179.8(6) |
| Bi1-N2-C6-C5 | -20.0(9) |
| C9-N2-C6-C7 | -0.6(7) |
| Bi1-N2-C6-C7 | 159.3(4) |
| C4-C5-C6-N2 | -0.6(10) |
| C4-C5-C6-C7 | -179.6(6) |
| N2-C6-C7-C8 | 0.4(7) |
| C5-C6-C7-C8 | 179.6(6) |
| N2-C6-C7-C27 | -177.4(6) |
| C5-C6-C7-C27 | 1.8(10) |
| C6-C7-C8-C9 | -0.1(7) |
| C27-C7-C8-C9 | 177.7(6) |
| C6-C7-C8-C30 | -179.3(7) |
| C27-C7-C8-C30 | -1.5(11) |
| C6-N2-C9-C10 | 178.3(5) |
| Bi1-N2-C9-C10 | 15.7(7) |
| C6-N2-C9-C8 | 0.5(7) |
| Bi1-N2-C9-C8 | -162.1(4) |
| C7-C8-C9-N2 | -0.3(7) |
| C30-C8-C9-N2 | 178.9(7) |
| C7-C8-C9-C10 | -177.8(6) |
| C30-C8-C9-C10 | 1.4(12) |
| C11-N3-C10-C9 | -178.2(5) |
| Bi1-N3-C10-C9 | -9.5(7) |
| N2-C9-C10-N3 | -3.2(9) |
| C8-C9-C10-N3 | 174.1(6) |
| C10-N3-C11-C16 | -179.2(5) |
| Bi1-N3-C11-C16 | 12.7(7) |
| C10-N3-C11-C12 | 1.4(9) |
| Bi1-N3-C11-C12 | -166.7(4) |
| N3-C11-C12-C13 | 179.9(5) |
| C16-C11-C12-C13 | 0.5(9) |
| C31-O1-C13-C12 | 6.4(9) |
| C31-O1-C13-C14 | -172.9(6) |

| | |
|---|---|
| C11-C12-C13-O1 | -179.4(6) |
| C11-C12-C13-C14 | -0.2(9) |
| C32-O2-C14-C15 | -4.6(9) |
| C32-O2-C14-C13 | 175.0(5) |
| O1-C13-C14-C15 | 178.5(5) |
| C12-C13-C14-C15 | -0.8(9) |
| O1-C13-C14-O2 | -1.2(8) |
| C12-C13-C14-O2 | 179.5(5) |
| O2-C14-C15-C16 | -178.9(5) |
| C13-C14-C15-C16 | 1.5(9) |
| C17-N4-C16-C11 | 176.8(5) |
| Bi1-N4-C16-C11 | -13.0(7) |
| C17-N4-C16-C15 | -3.6(9) |
| Bi1-N4-C16-C15 | 166.6(4) |
| N3-C11-C16-N4 | 0.3(8) |
| C12-C11-C16-N4 | 179.7(5) |
| N3-C11-C16-C15 | -179.3(5) |
| C12-C11-C16-C15 | 0.1(8) |
| C14-C15-C16-N4 | 179.4(5) |
| C14-C15-C16-C11 | -1.1(8) |
| C16-N4-C17-C18 | 179.3(5) |
| Bi1-N4-C17-C18 | 8.7(7) |
| C21-N5-C18-C17 | 178.0(5) |
| Bi1-N5-C18-C17 | -13.2(7) |
| C21-N5-C18-C19 | -1.1(7) |
| Bi1-N5-C18-C19 | 167.8(4) |
| N4-C17-C18-N5 | 2.3(8) |
| N4-C17-C18-C19 | -178.9(6) |
| N5-C18-C19-C20 | 1.4(7) |
| C17-C18-C19-C20 | -177.5(6) |
| N5-C18-C19-C33 | -179.9(6) |
| C17-C18-C19-C33 | 1.2(10) |
| C18-C19-C20-C21 | -1.1(7) |
| C33-C19-C20-C21 | -179.7(6) |
| C18-C19-C20-C34 | -177.3(7) |
| C33-C19-C20-C34 | 4.1(12) |

| | |
|---|---|
| C18-N5-C21-C22 | -179.3(5) |
| Bi1-N5-C21-C22 | 14.3(8) |
| C18-N5-C21-C20 | 0.3(6) |
| Bi1-N5-C21-C20 | -166.1(4) |
| C19-C20-C21-N5 | 0.5(7) |
| C34-C20-C21-N5 | 176.8(6) |
| C19-C20-C21-C22 | -179.9(6) |
| C34-C20-C21-C22 | -3.6(11) |
| N5-C21-C22-C1 | -0.7(9) |
| C20-C21-C22-C1 | 179.8(6) |
| N1-C1-C22-C21 | 1.8(10) |
| C2-C1-C22-C21 | 179.7(5) |
| C3-C2-C23-C24 | -94.0(8) |
| C1-C2-C23-C24 | 83.1(8) |
| C2-C3-C25-C26 | 96.8(8) |
| C4-C3-C25-C26 | -83.6(8) |
| C8-C7-C27-C28 | -87.4(9) |
| C6-C7-C27-C28 | 90.0(8) |
| C7-C27-C28-C29 | -159.2(7) |
| C27-C28-C29-O4 | 81.3(10) |
| C19-C20-C34-C35 | 105.5(9) |
| C21-C20-C34-C35 | -70.1(10) |
| C20-C34-C35-C36 | 175.1(8) |
| C34-C35-C36-O3 | 81.7(8) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

**Figure 1.** View of the Bi coordination to the macrocycle in **2a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Note that this structure shows only one individual texaphyrin subunit viewed from the top (ancillary ligands disregarded). The complete structure is shown in Figure2.

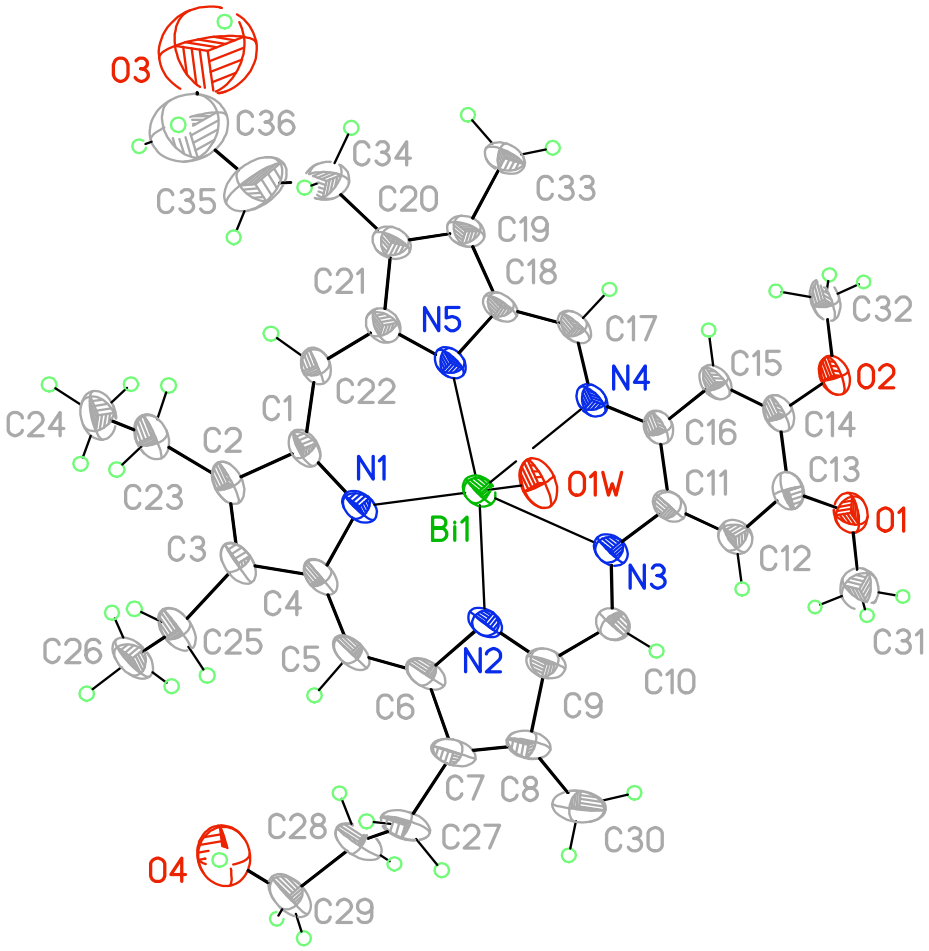
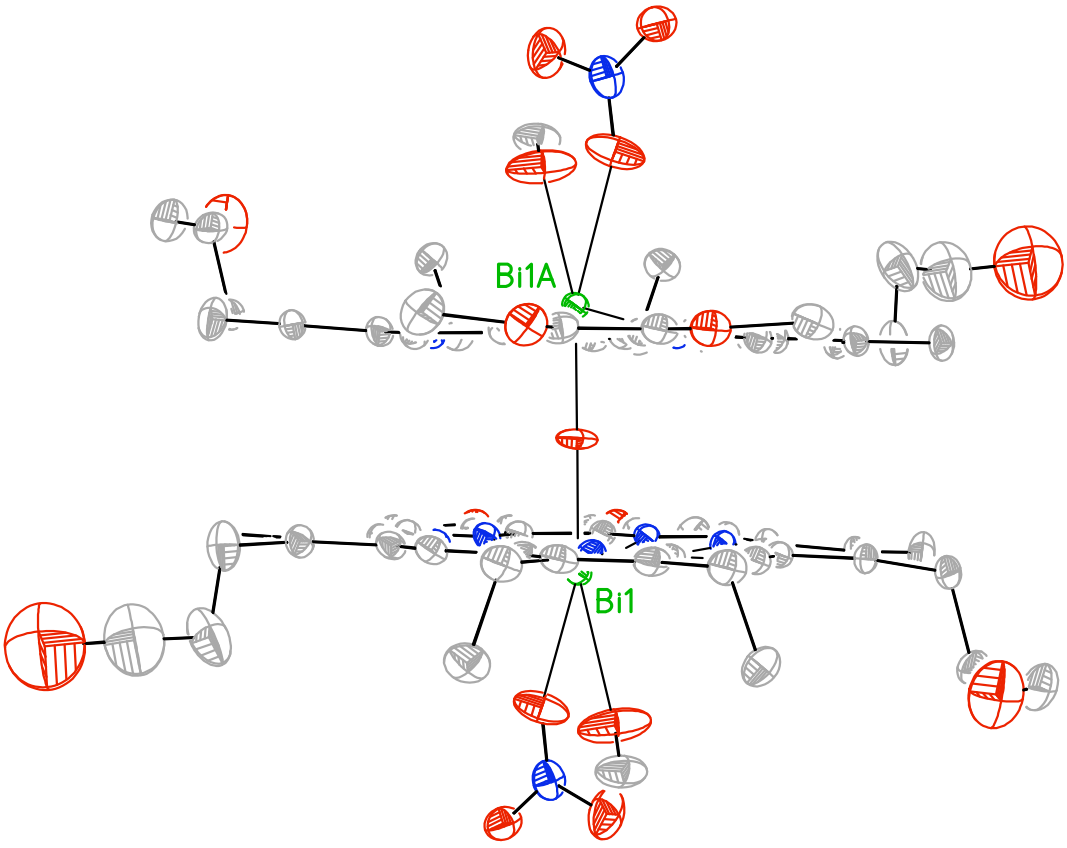


**Figure 2.** View of the dimer present in **2a**. Displacement ellipsoids are scaled to the 50% probability level. The oxygen atom bridging the two Bi ions resides on a crystallographic inversion center at ½, ½, 0. The distance between the rings defined by the five nitrogen atoms of the macrocycles is 3.433(5) Å.



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9. $R_w(F^2) = \{Sw(|F_o|^2 - |F_c|^2)^2/Sw(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
   $R(F) = S(|F_o| - |F_c|)/S|F_o|\}$ for reflections with $F_o > 4(s(F_o))$.

   $S = [Sw(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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