

Constructing Metal Nanoparticle Multilayers with Polyphenylene Dendrimer/Gold Nanoparticles via “Click” Chemistry

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Synthesis of 4-(Aminophenylethynyl)acetylene (2). 4-Iodoaniline (6 g, 27.4 mmol), copper(I) iodide (0.5434 g, 2.85 mmol), triphenylphosphane (0.4347 g, 2.86 mmol), and Pd(PPh₃)₂Cl₂ catalyst (0.9931 g, 1.39 mmol) were dissolved in a mixture of dry THF (60 mL) and triethylamine (35 mL) at room temperature with exclusion of light, where the exhausting-refilling process was carried out for three times. After 10 min stirring, trimethylsilylacetylene (TMSA, 4.5 mL, 31.7 mmol) was injected dropwise to this solution. After 4 h, the reaction mixture was filtered and then extracted several times with dichloromethane. The organic phase was washed with distilled water, dried over anhydrous MgSO₄, and purified by column chromatography with dichloromethane and petroleum ester (v/v, 2:1, R_f = 0.2) to afford 4-(aminophenylethynyl)trimethylsilane (4.80 g, 92% yield) as white crystal.

The resulting 4-(aminophenylethynyl)trimethylsilane (1.30 g, 6.87 mmol) in THF (30 mL) was added to MeOH (10 mL) solution of KOH (0.8036 g, 14.3 mmol). After 30 min stirring, dichloromethane (80 mL) was added, and the organic phase was washed with distilled water and dried over MgSO₄. After evaporating the solvent, the crude product was purified by column chromatography to afford **2** (0.619 g, 76.9%) as light yellow solid.

General Procedure for the Diels-Alder Reaction Between Tetraphenylcyclopentadienone and Aryl-ethynyl Derivatives. The reaction was carried out in a schlenk flask under argon. The reaction flask with the tetraphenylcyclopentadienone (**1**, 0.9612 g, 1.3 mmol) and aryl-ethynyl derivative (**2**, 0.1320 g, 1.1 mmol) solution in *o*-xylene (10 mL) was evacuated and filled with argon three times, and then the temperature was increased up to make the reaction solution reflux. The reaction was controlled by TLC, and the reaction time was dependent on the generation and varied from 16 h for **G1** to 20 h for **G2**. After cooling, the solvent was evaporated, and the compound was purified by column chromatography with dichloromethane and petroleum ester (v/v, 2:1, R_f = 0.30) as eluent to afford **G1**. The synthetic procedure of **G2** is similar with that of **G1**.

G1. Yield, 76%. FT-IR (KBr, cm⁻¹): 3461, 3385, 2153, 1621, 882. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.52-6.47 (m, 23 H); 2.99 (s, 2 H); 1.08 (s, 42 H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 144.6, 141.5, 141.1, 140.8, 140.7, 140.2, 139.9, 139.1, 137.6, 131.7, 131.5, 131.3, 130.9, 130.8, 130.6, 129.9,

127.8, 127.1, 126.4, 125.7, 120.6, 120.4, 114.5, 107.4, 107.3, 90.1, 89.9, 18.7, 11.4. Anal. Calcd for $C_{58}H_{67}NSi_2$: C, 83.49; H, 8.09; N, 1.68. Found: C, 83.12; H, 8.18; N, 1.62.

G2. Yield, 63%. HRMS (EI) calcd. for $C_{140}H_{147}NSi_4Na^+$ $[M+Na]^+$, 1977.0508; found, 1977.0503. FT-IR (KBr, cm^{-1}): 3470, 3380; 2150; 1620; 883. 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-6.45 (m, 61 H); 1.58 (s, 2 H); 1.09 (d, 84 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.3-114.6, 107.4, 107.3, 90.1, 90.0, 18.68, 11.4. Anal. Calcd for $C_{140}H_{147}NSi_4$: C, 85.97; H, 7.57; N, 0.72. Found: C, 85.76; H, 7.48; N, 0.69.

General Procedure for the Desilylation of Triisopropylsilyl (TiPS) Substituted Polyphenylene Dendrimers. Triisopropylsilyl-substituted polyphenylene dendrimers (**G1**, 0.5455 g, 0.65 mmol) and tetrabutylammonium fluoride trihydrate (1.5 mol $Bu_4N^+F^-$ per triisopropylsilyl group) in THF (1.8 mL) were added to THF (6 mL), and then the temperature was increased to reflux. After 5 h, CH_2Cl_2 (25 mL) was added, and the organic phase was washed with water and dried over $MgSO_4$. After evaporating the solvent, the crude product was purified by column chromatography (0.2963 g, 87.4%).

3. FT-IR (KBr, cm^{-1}): 3450, 3382; 3286; 2105; 1620. 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-6.52 (m, 23H); 2.99 (s, 2H); 1.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 144.6, 141.3, 141.2, 140.8, 140.7, 140.6, 139.8, 139.1, 137.6, 131.7, 131.6, 131.5, 131.4, 130.9, 130.8, 130.7, 129.8, 129.7, 127.8, 127.2, 126.4, 125.7, 119.2, 118.9, 114.5, 83.9, 83.8. Anal. Calcd for $C_{40}H_{27}N$: C, 92.10; H, 5.22; N, 2.69. Found: C, 91.97; H, 5.18; N, 2.26.

Synthesis of Compound 4. 6-Bromohexanoyl chloride was prepared by reaction of 6-bromohexanoic acid and thionyl chloride at 70 °C for 4 h. A 6-bromohexanoyl chloride (0.427g 0.2 mmol) and **G2** (0.1001 g, 0.05 mmol) in $CHCl_3$ (6 mL) solution was added into a three-necks round flask. The mixture was filled with argon. 2 mL triethylamine (TEA) was added to the mixture and stirred at 0 °C for 1 h. Then the mixture was sequentially stirred at room temperature overnight. The mixture was concentrated and poured into a 5% HCl aqueous solution (10 mL) and extracted with chloroform three times. The organic phase was washed with water, dried over anhydrous $NaSO_4$, and evaporated. By column chromatography (v/v, dichloromethane:petroleum ester = 2:1, R_f = 0.20) **4** was obtained as yellow solid

(0.09 g, 90 %). HRMS (EI) calcd. for $C_{146}H_{156}BrNOSi_4Na^+$ $[M+Na]^+$, 2153.0345; found, 2153.0308. FT-IR (KBr, cm^{-1}): 3420; 2940, 2860; 2150; 1700; 883. 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-6.45 (m, 62 H); 3.42 (t, 2 H); 2.34 (t, 2 H); 1.94-1.87 (m, 2 H); 1.76-1.72 (m, 2 H); 1.57-1.48 (m, 2 H); 1.09 (d, 84 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 170.9-118.8, 107.4, 107.3, 90.1, 90.0, 37.5, 33.5, 32.4, 27.7, 24.6, 18.7, 11.3. Anal. Calcd for $C_{146}H_{156}BrNOSi_4$: C, 82.21; H, 7.37; N, 0.66. Found: C, 82.58; H, 7.21; N, 0.69.

Synthesis of Compound 5. A solution of **4** (0.3376 g, 0.16 mmol) in THF (10 mL) was added to a solution of potassium thioacetate (0.0966 g, 0.85 mmol) in EtOH (2 mL) and refluxed under argon for 4h. The resulting reaction mixture was concentrated and extracted three times with $CHCl_3$ and water. The organic layer was dried over anhydrous Na_2SO_4 . After evaporation, the residue was purified by column chromatography on silica gel eluted with CH_2Cl_2 as eluent and gave **5** (R_f = 0.30) (0.2765 g, 82 %). HRMS (EI) calcd. for $C_{148}H_{159}NO_2SSi_4Na^+$ $[M+Na]^+$, 2149.1066; found, 2149.1083. FT-IR (KBr, cm^{-1}): 3360; 2150; 1710; 883. 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-6.46 (m, 62H), 2.87 (t, 2H), 2.32 (t, 5H), 1.74-1.72 (m, 2H), 1.64-1.62 (m, 2H), 1.46-1.44 (m, 2H), 1.10 (s, 84H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 196.2-118.8, 107.4, 107.3, 90.1, 90.0, 37.4, 30.7, 29.7, 29.3, 28.8, 24.9, 18.7, 11.4. Anal. Calcd for $C_{148}H_{159}NO_2SSi_4$: C, 83.52; H, 7.53; N, 0.66. Found: C, 83.74; H, 7.82; N, 0.61.

Synthesis of G2SH. To a THF solution (10 mL) of **5** (0.3166 g, 0.15 mmol), a MeOH solution (13 mL) of potassium hydroxide (0.0688 g, 1.2 mmol) was added and the mixture was refluxed under argon for 30 min. The resulting reaction mixture was evaporated and extracted three times with $CHCl_3$ and water, and dried over Na_2SO_4 . After removal of the solvent, the residue was purified by column chromatography with dichloromethane and petroleum ester (v/v, 30:1, R_f = 0.20) as eluent and gave G2SH (0.2055 g, 65%). FT-IR (KBr, cm^{-1}): 3360; 2150; 1700; 883. 1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48-6.45 (m, 62 H); 2.68 (t, 2 H); 2.32 (t, 2 H); 1.72 (m, 4 H); 1.58 (t, 2 H); 1.48-1.44 (m, 2H); 1.10 (m, 84 H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ = 171.1-118.9, 107.4, 107.3, 90.1, 90.0, 37.5, 31.9, 29.3, 27.2, 25.1, 18.7, 11.4. Anal. Calcd for $C_{146}H_{157}NOSSi_4$: C, 84.05; H, 7.59; N, 0.67. Found: C, 83.84; H, 7.63; N, 0.68.

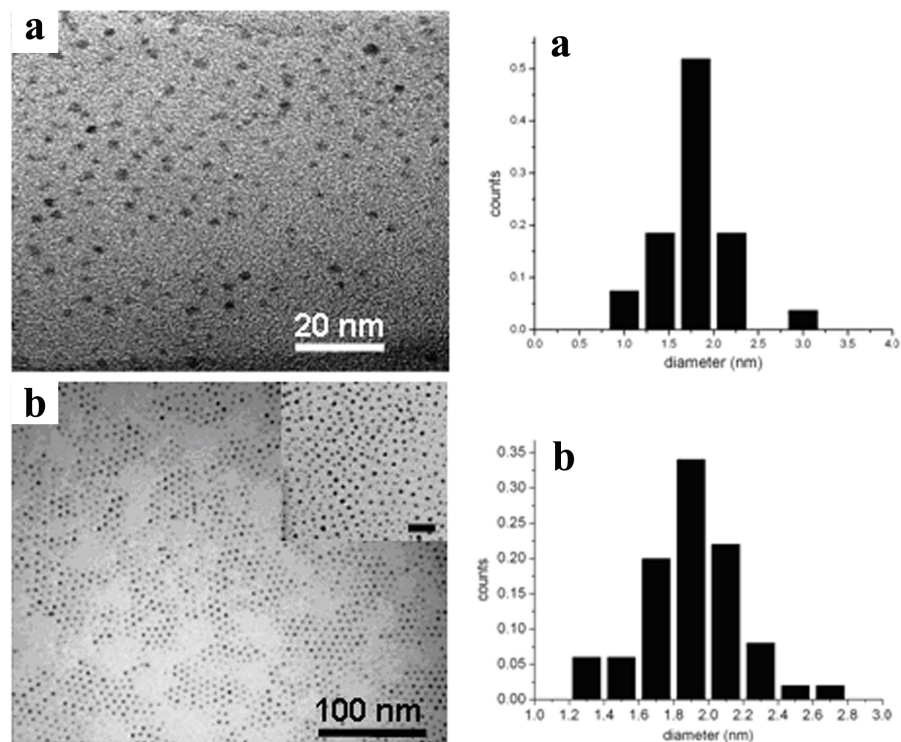


Figure S1. TEM images and size distributions of G2SH-AuNPs with the ratio of (a) $\text{AuCl}_4^-/\text{thiol} = 1$, (b) $\text{AuCl}_4^-/\text{thiol} = 2$. The scale bar of insert image is 20 nm.

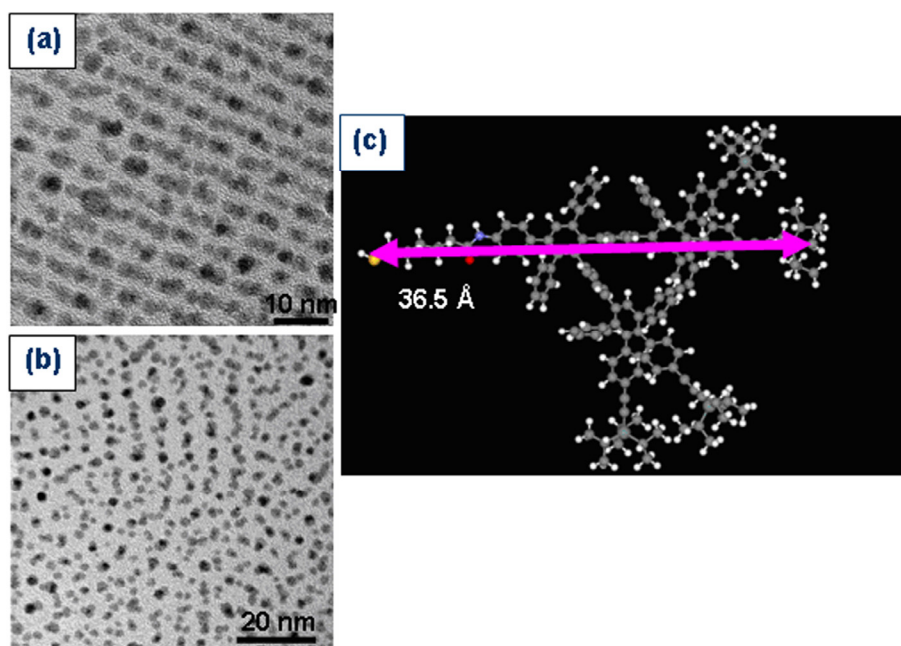


Figure S2. TEM images and Gaussian simulation (c) of G2SH-AuNPs with the ratio of (a) $\text{AuCl}_4^-/\text{thiol} = 4$, (b) $\text{AuCl}_4^-/\text{thiol} = 5$.

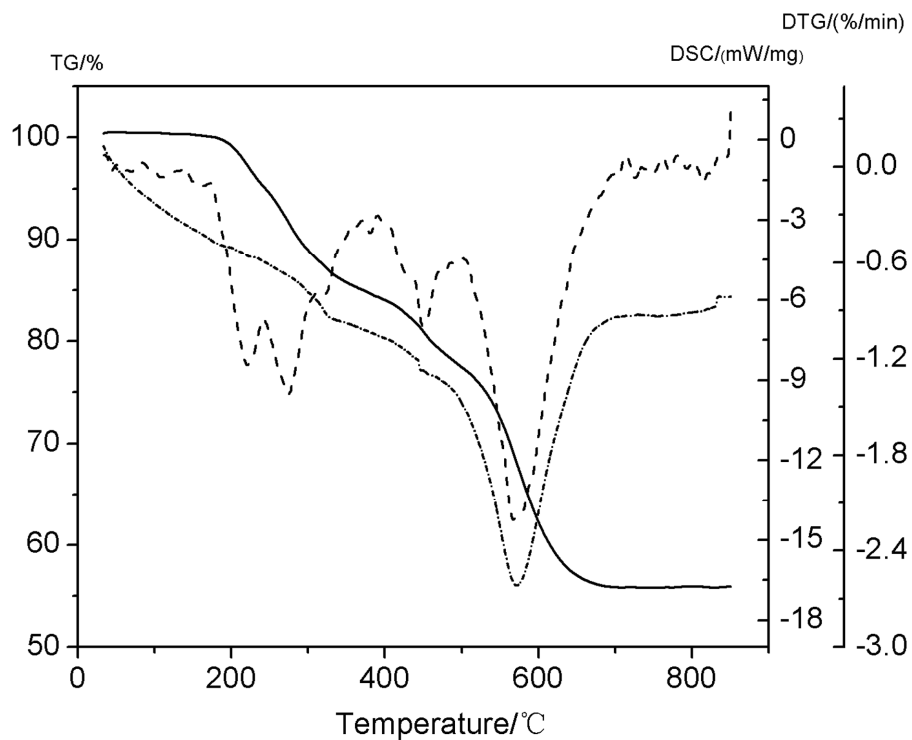


Figure S3. TGA analysis of G2SH-AuNPs with the ratio of $\text{AuCl}_4^-/\text{thiol} = 4$.

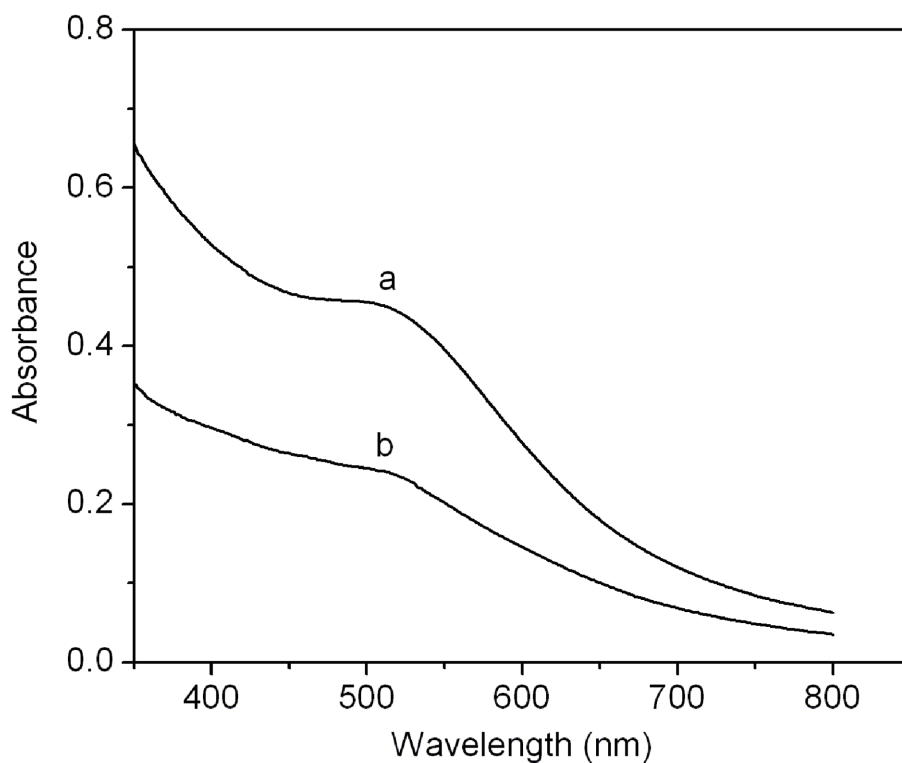


Figure S4. UV-vis spectra of Preparation of G2SH-AuNPs with the ratio of $\text{AuCl}_4^-/\text{thiol} = 3$ before (a) and after (b) deprotection.

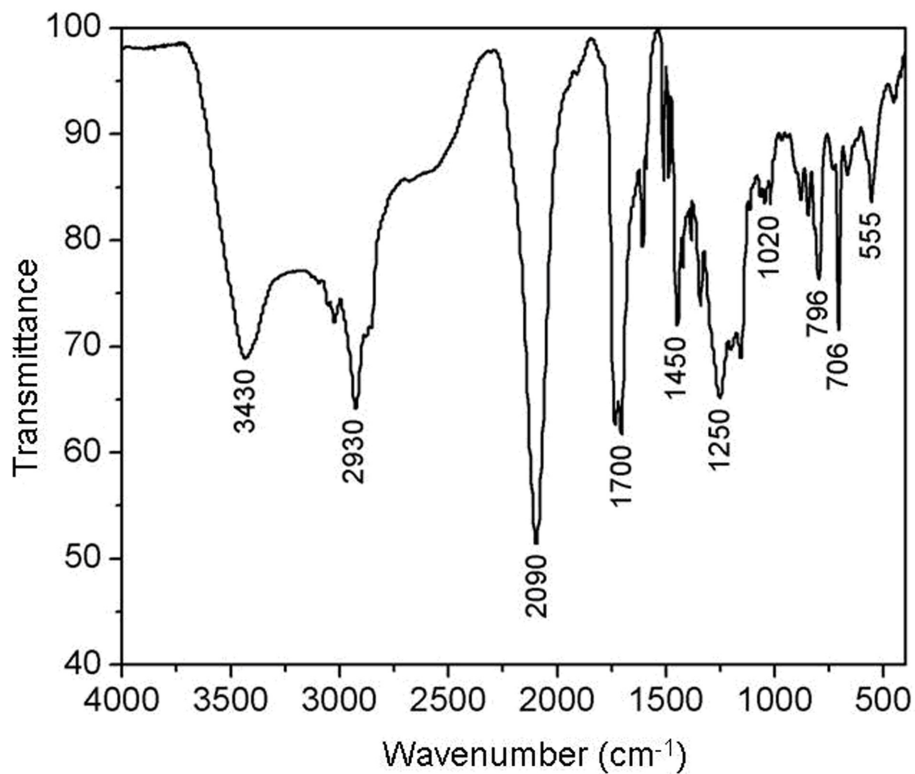


Figure S5. FT-IR spectra of P(VBA-AA).

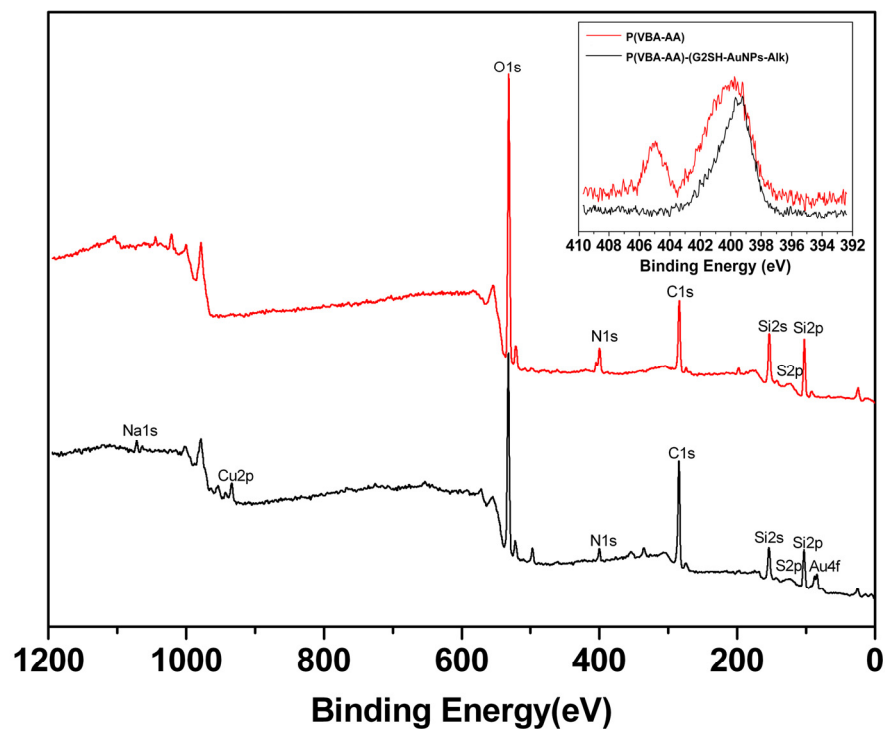


Figure S6. High-resolution XPS spectra of the P(VBA-AA) (red) and P(VBA-AA)-(G2SH-AuNPs-Alk) (black). Insert: XPS spectra amplification from 392 to 410 eV.

Instrument:



IonSpec 4.7 Tesla FTMS

Card Serial Number: I101848

Sample Serial Number: LX-100926K

Operator : HuaQin Date: 2010/10/25

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 2153.0290 \pm 0.005

Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	150
H	1.007825	0	160
N	14.003074	0	1
O	15.994915	0	1
Si	27.976927	0	4
Br	78.918338	0	1
Na	22.989770	0	1

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer

Minimum DBE = 0

Search Results:

Number of Hits = 2

m/z	Delta m/z	DBE	Formula
2153.03081	-0.00181	75.5	C ₁₅₀ H ₁₅₂ NSi ₃ BrNa ⁺¹
2153.03396	-0.00496	69.5	C ₁₄₆ H ₁₅₆ NOSi ₄ BrNa ⁺¹

Instrument:



IonSpec 4.7 Tesla FTMS

Card Serial Number: I101982

Sample Serial Number: L-101012

Operator : HuaQin Date: 2010/11/11

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 2149.1075 \pm 0.005

Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	150
H	1.007825	0	160
N	14.003074	0	1
O	15.994915	0	3
Si	27.976927	0	5
S	31.972071	0	1
Na	22.989770	0	1

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer

Minimum DBE = 0

Search Results:

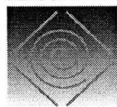
Number of Hits = 5

m/z	Delta m/z	DBE	Formula
2149.10826	-0.00076	71.5	C ₁₄₉ H ₁₅₈ NO ₃ Si ₅ ⁺¹
2149.10848	-0.00098	72.5	C ₁₅₀ H ₁₅₈ NO ₂ Si ₄ S ⁺¹
2149.10608	0.00142	70.0	C ₁₄₈ H ₁₅₉ NO ₂ Si ₄ SNa ⁺¹
2149.10585	0.00165	69.0	C ₁₄₇ H ₁₅₉ NO ₃ Si ₅ Na ⁺¹
2149.10307	0.00443	71.0	C ₁₅₀ H ₁₆₀ OSi ₅ S ⁺¹

Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT



Instrument:



IonSpec 4.7 Tesla FTMS

Card Serial Number: I101846

Sample Serial Number: LX-100926J

Operator : HuaQin Date: 2010/10/25

Operation Mode: MALDI/DHB

Elemental Composition Search Report:

Target Mass:

Target m/z = 1977.0493 \pm 0.004

Charge = +1

Possible Elements:

Element:	Exact Mass:	Min:	Max:
C	12.000000	0	150
H	1.007825	0	150
N	14.003074	0	5
Si	27.976927	0	5
Na	22.989770	0	1

Additional Search Restrictions:

DBE Limit Mode = Both Integer and Half-Integer

Minimum DBE = 0

Search Results:

Number of Hits = 5

m/z	Delta m/z	DBE	Formula
1977.05028	-0.00098	68.0	C ₁₄₀ H ₁₄₇ NSi ₄ Na ⁺¹
1977.05208	-0.00278	62.5	C ₁₃₄ H ₁₄₉ N ₄ Si ₅ Na ⁺¹
1977.05215	-0.00285	138.0	C ₁₄₇ H ₂₂ N ₂ Si ₅ Na ⁺¹
1977.05255	-0.00325	75.5	C ₁₄₄ H ₁₄₁ N ₂ Si ₂ Na ⁺¹
1977.05268	-0.00338	70.5	C ₁₄₂ H ₁₄₆ NSi ₄ ⁺¹

High Resolution MS Data Report of G2