

Supporting information:**Inter-staple Dithiol Crosslinking in Au₂₅(SR)₁₈ Nanomolecules: A Combined Mass Spectrometric and Computational Study**

Vijay Reddy Jupally, † Rajesh Kota, † Eric Van Dornshuld, † Daniell L. Mattern, † Gregory S. Tschumper, † De-en Jiang, § Amala Dass*, †

NMR Spectra

Supporting Figure 1. ¹H NMR for (3)

Supporting Figure 2. ¹³C NMR for (3)

Supporting Figure 3. ¹H NMR for (4)

Supporting Figure 4. ¹³C NMR for (4)

Supporting Figure 5. ¹H NMR for (5)

Supporting Figure 6. ¹³C NMR for (5)

Supporting Figure 7 & 8. Raw MALDI data for Figure 1

Supporting Figure 9 & 10. Raw MALDI data for Figure 2

Supporting Figure 11 & 12. Raw MALDI data for Figure 3

Supporting Figure 13 & 14. Raw MALDI data for Figure 4

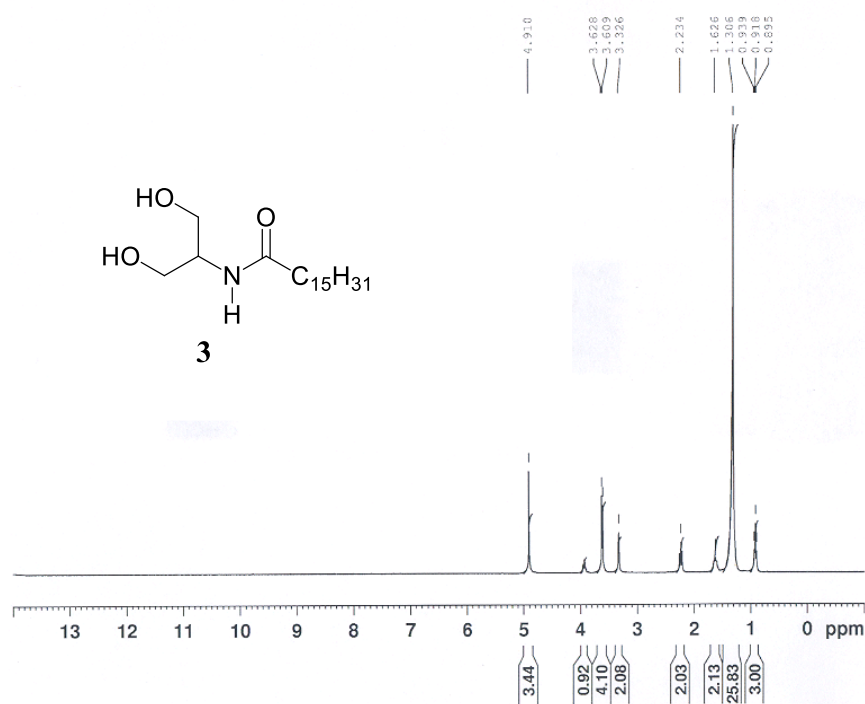
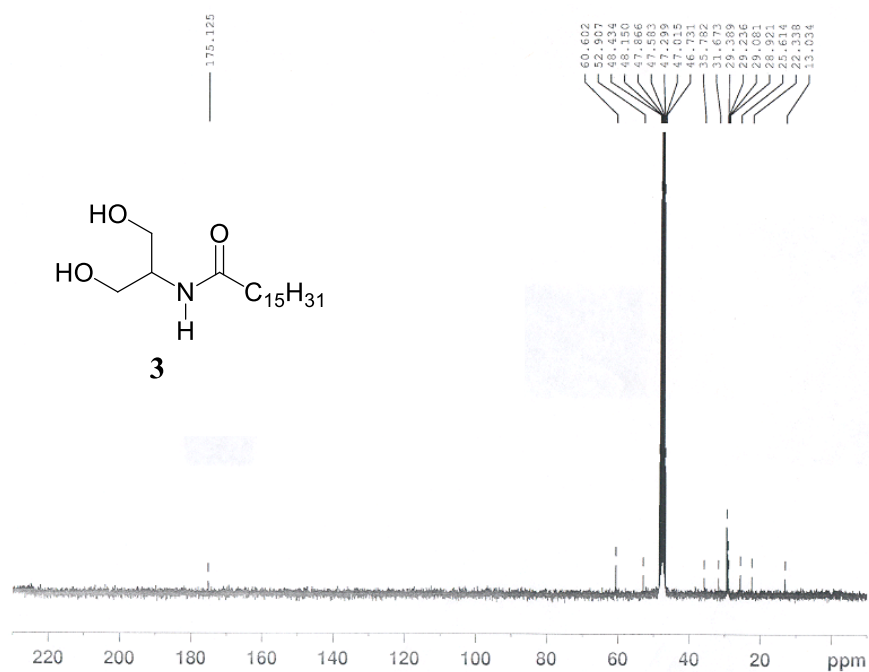
Supporting Figure 15 & 16. Raw MALDI data for Figure 5

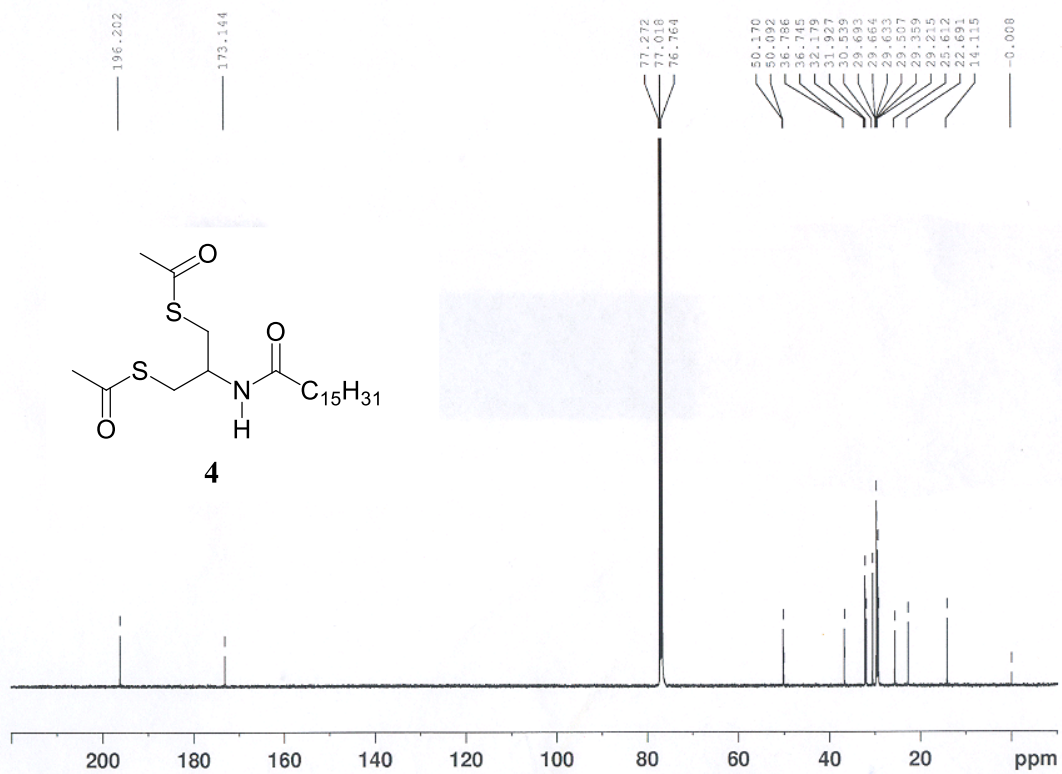
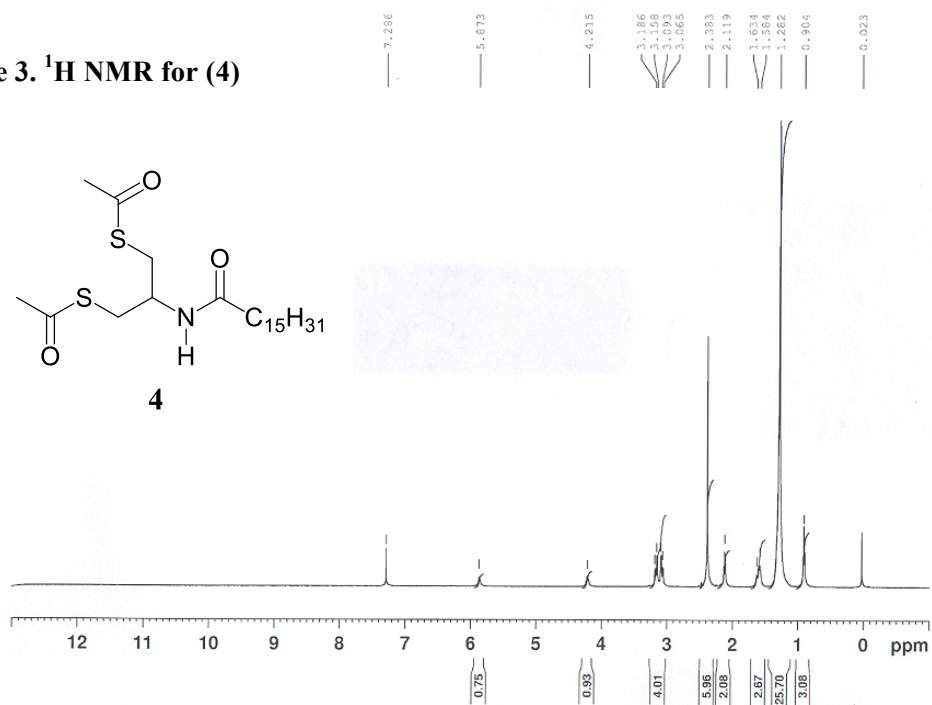
Supporting Figure 17 & 18. Raw MALDI data for Figure 10

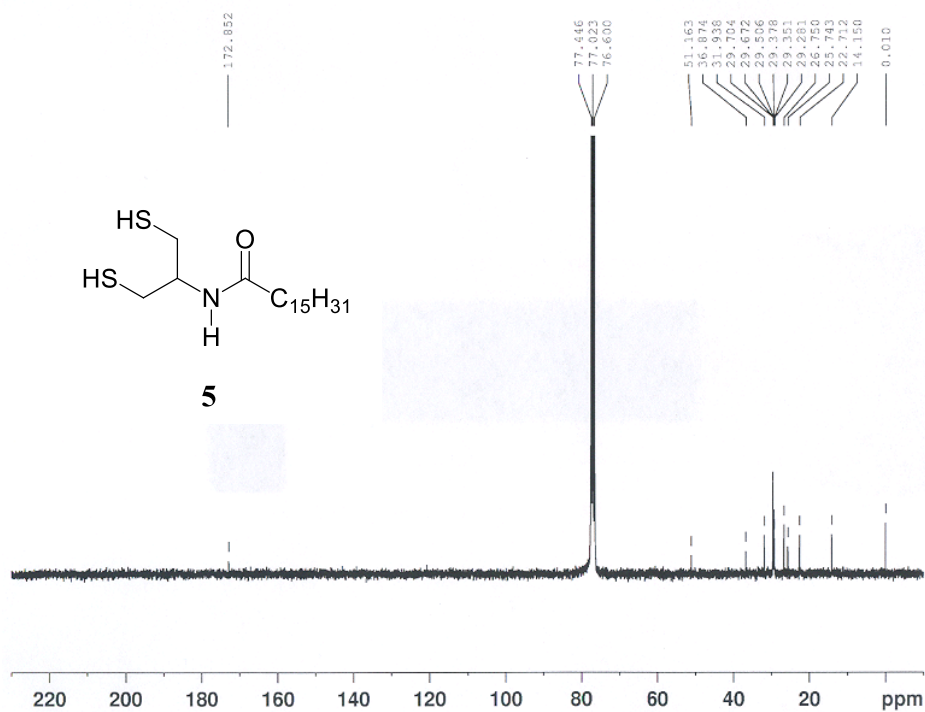
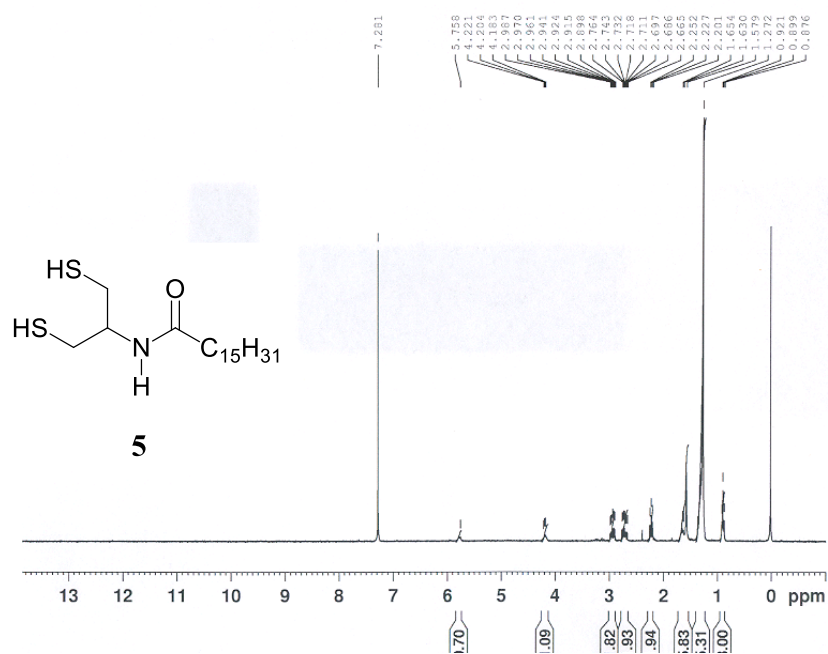
Supporting Figure 19 & 20. Raw MALDI data for Figure 11

Supporting Figure 21 & 22. Raw MALDI data for Figure 13

NMR Spectra

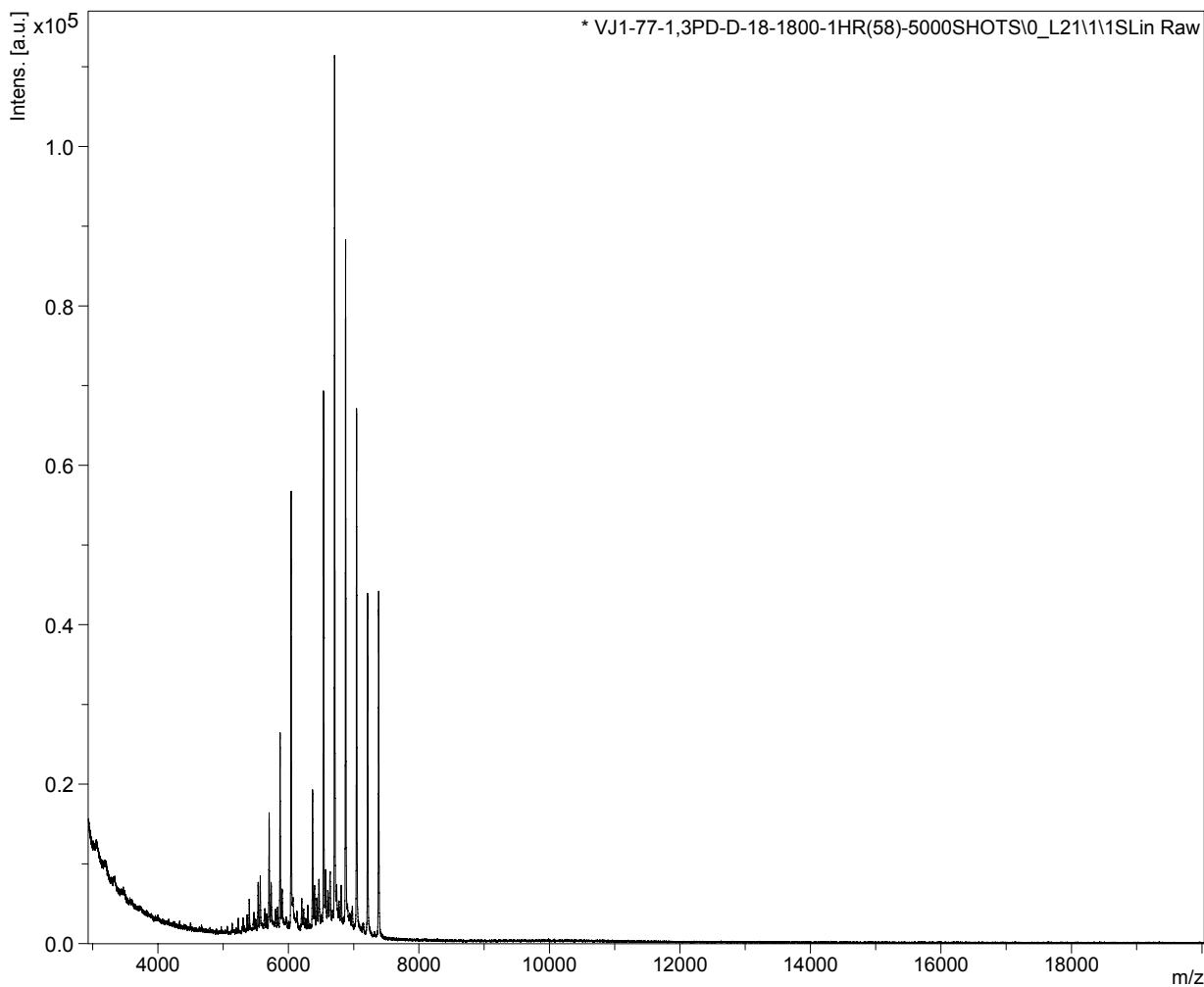
Supporting Figure 1. ¹H NMR for (3)Supporting Figure 2. ¹³C NMR for (3)

Supporting Figure 3. ^1H NMR for (4)Supporting Figure 4. ^{13}C NMR for (4)



Supporting Figure 7. MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,3-propanedithiol. Figure 1 in the manuscript is extracted from this data.

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S\0_L21\1



Acquisition Parameter

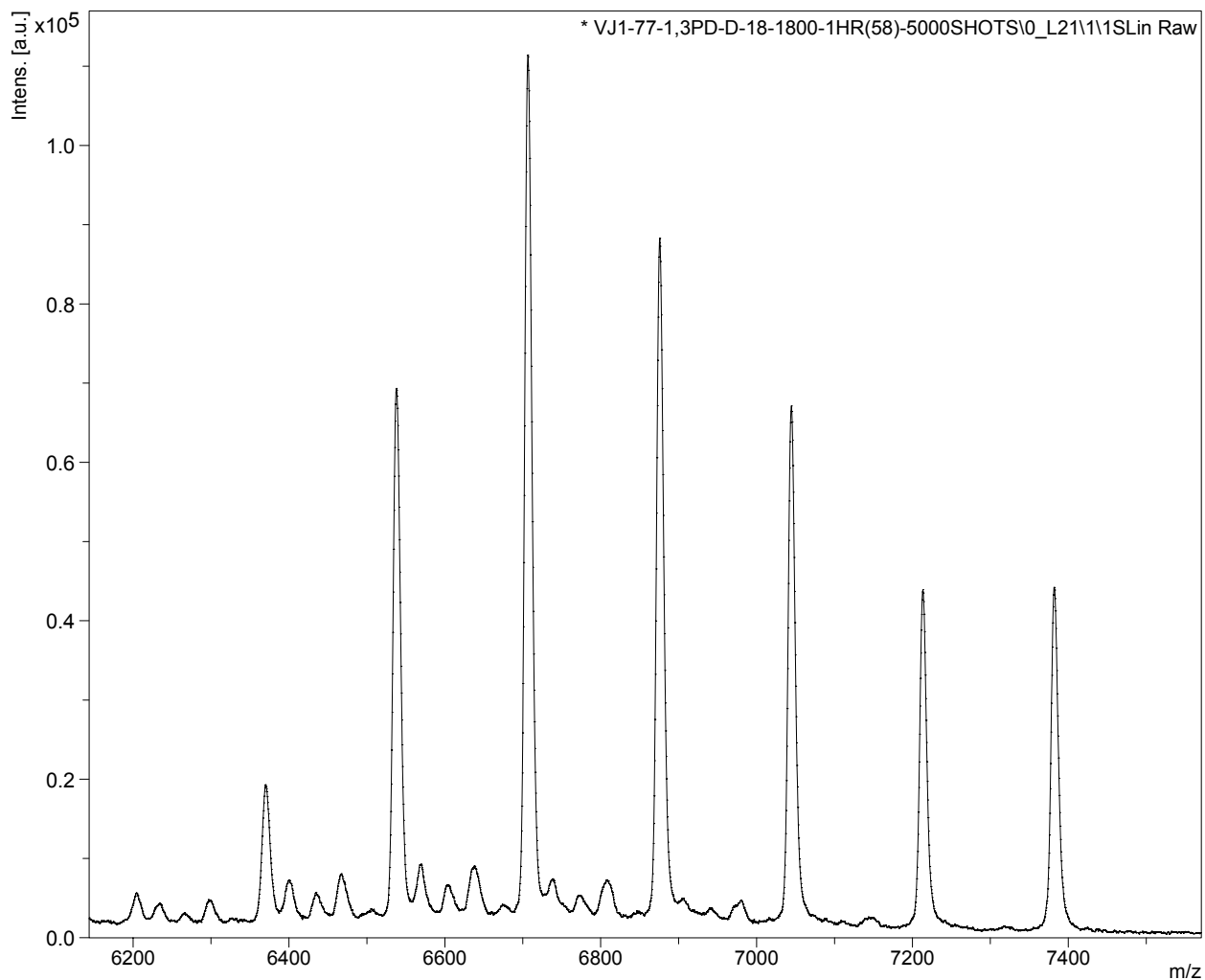
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Acquisition mode	qsim
Acquisition operation mode	Linear
Voltage polarity	POS
Number of shots	5000
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 8. Expanded MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,3-propanedithiol. Figure 1 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\101018\VJ1-77-1,3PD-D-18-1800\VJ1-77-1,3PD-D-18-1800-1HR(58)-5000SHOT S\0_L21\1



Acquisition Parameter

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Name of spectrum used for calibration	
Calibration reference list used	

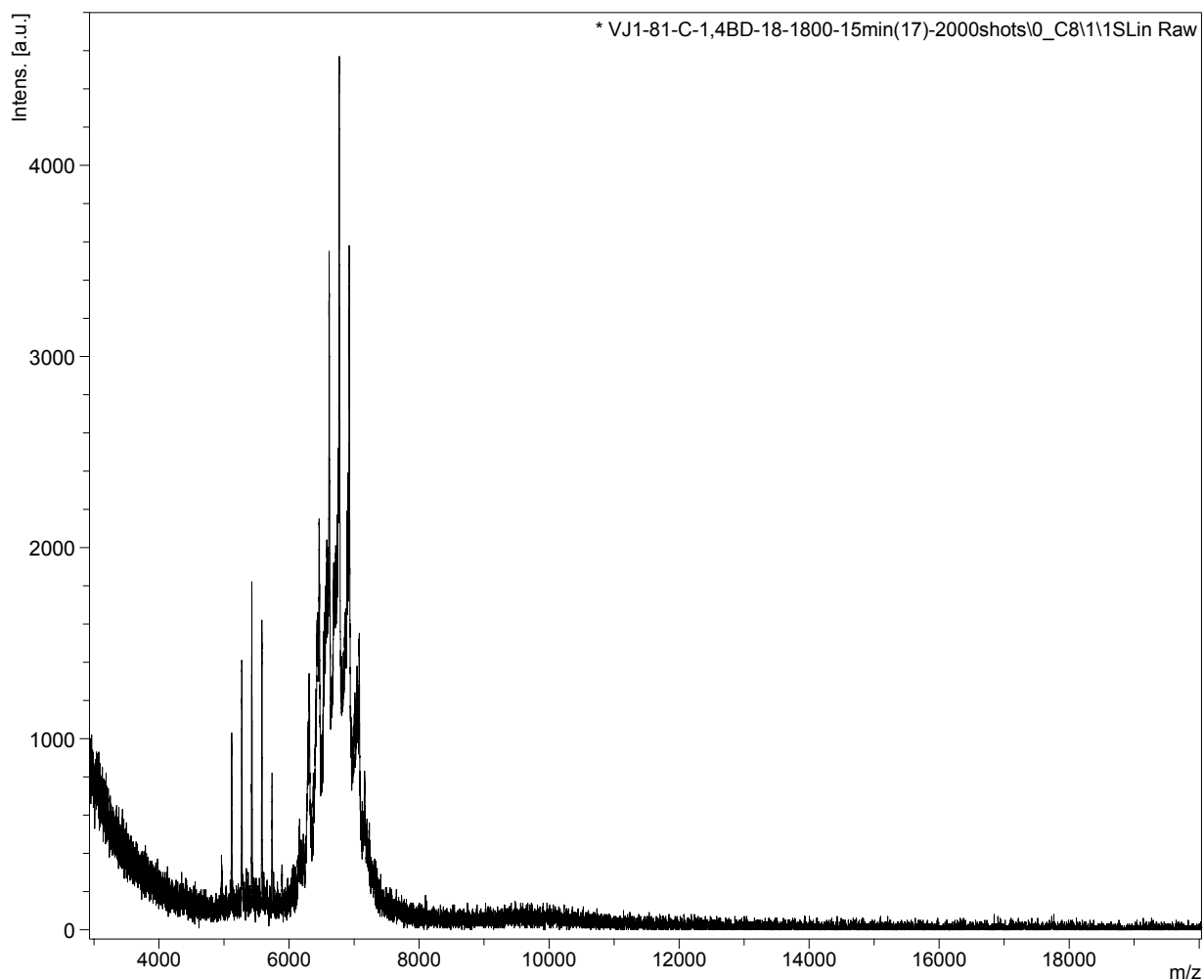
Instrument Info

Instrument type	autoflex
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Supporting Figure 9. MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol. Figure 2 in the manuscript is extracted from this data.

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Acquisition Parameter

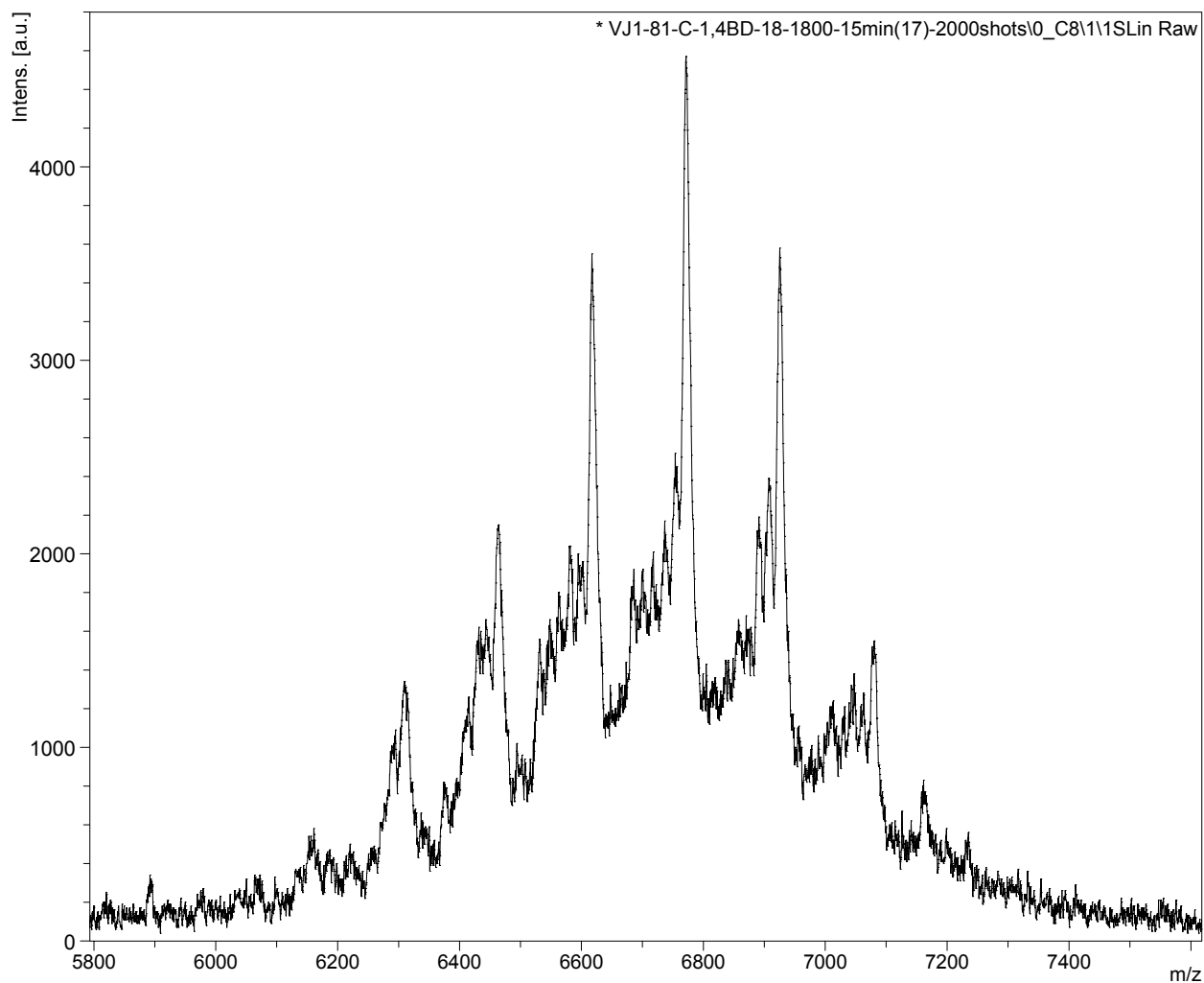
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Number of shots	2000
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 10. Expanded MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol. Figure 2 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\101028\VJ1-81-C-1,4BD-18-1800\VJ1-81-C-1,4BD-18-1800-15min(17)-2000shots\0_C8\1



Acquisition Parameter

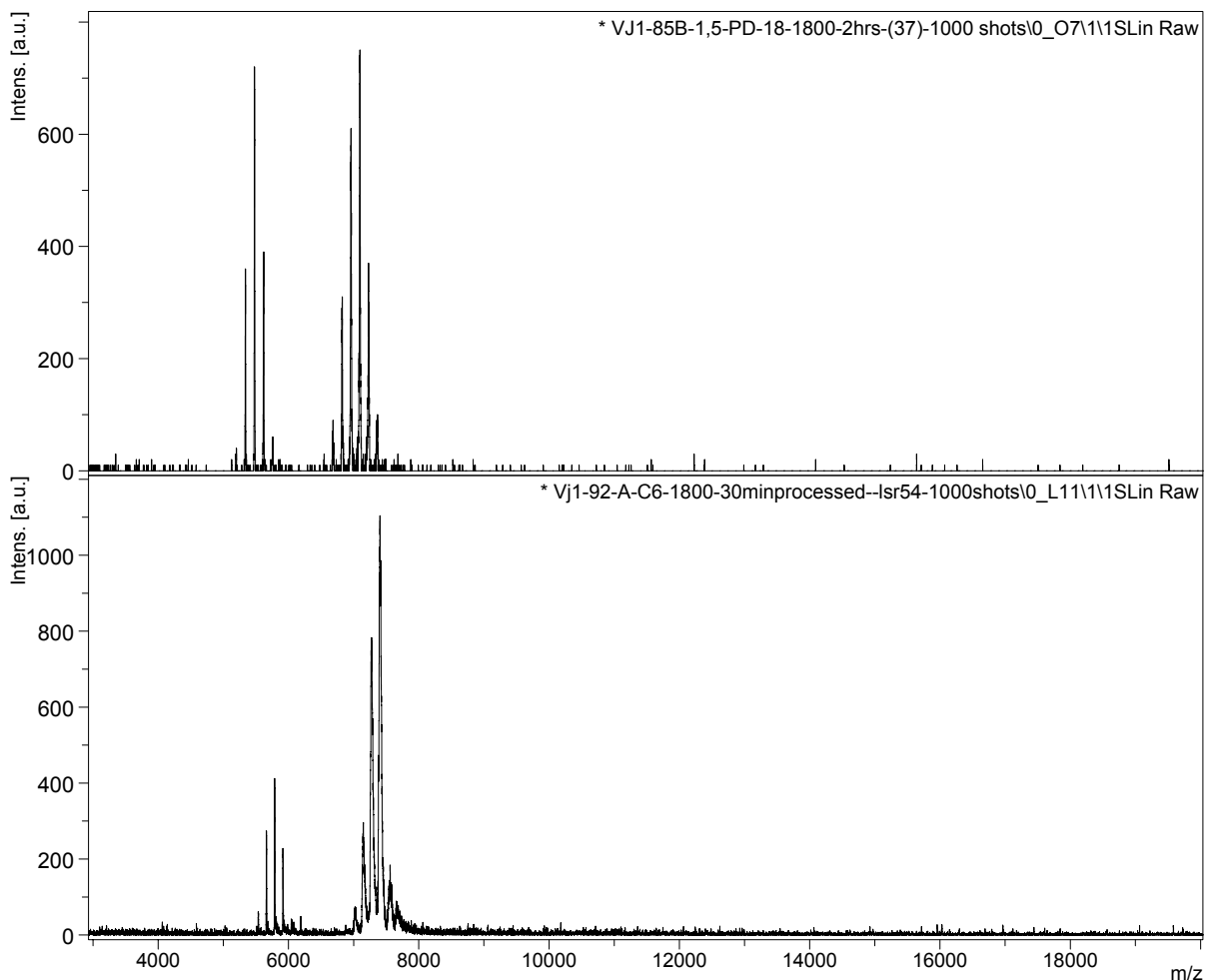
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Number of shots	2000
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 11. MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,5-pentanedithiol (top) and 1,6-hexanedithiol (bottom). Figure 3 in the manuscript is extracted from this data.



Acquisition Parameter

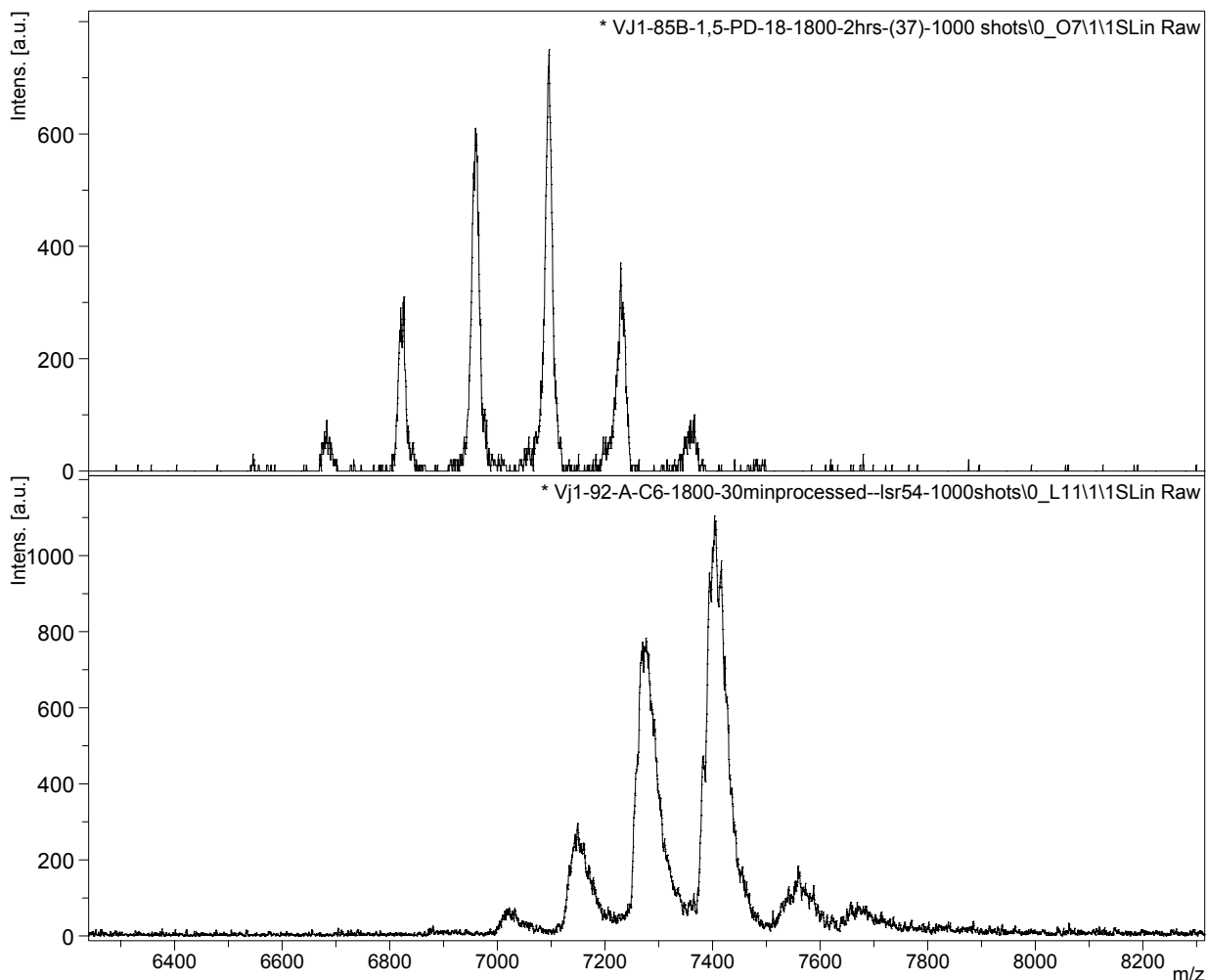
Date of acquisition
Acquisition method name
Acquisition mode
Acquisition operation mode
Voltage polarity
Number of shots
Name of spectrum used for calibration
Calibration reference list used

Instrument Info

Instrument type

Supporting Figure 12. Expanded MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,5-pentanedithiol (top) and 1,6-hexanedithiol (bottom). Figure 3 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\110117_C6\VJ1-92-A-C6-1800\Vj1-92-A-C6-1800-30minprocessed--Isr54-1000shots\0_L11\1



Acquisition Parameter

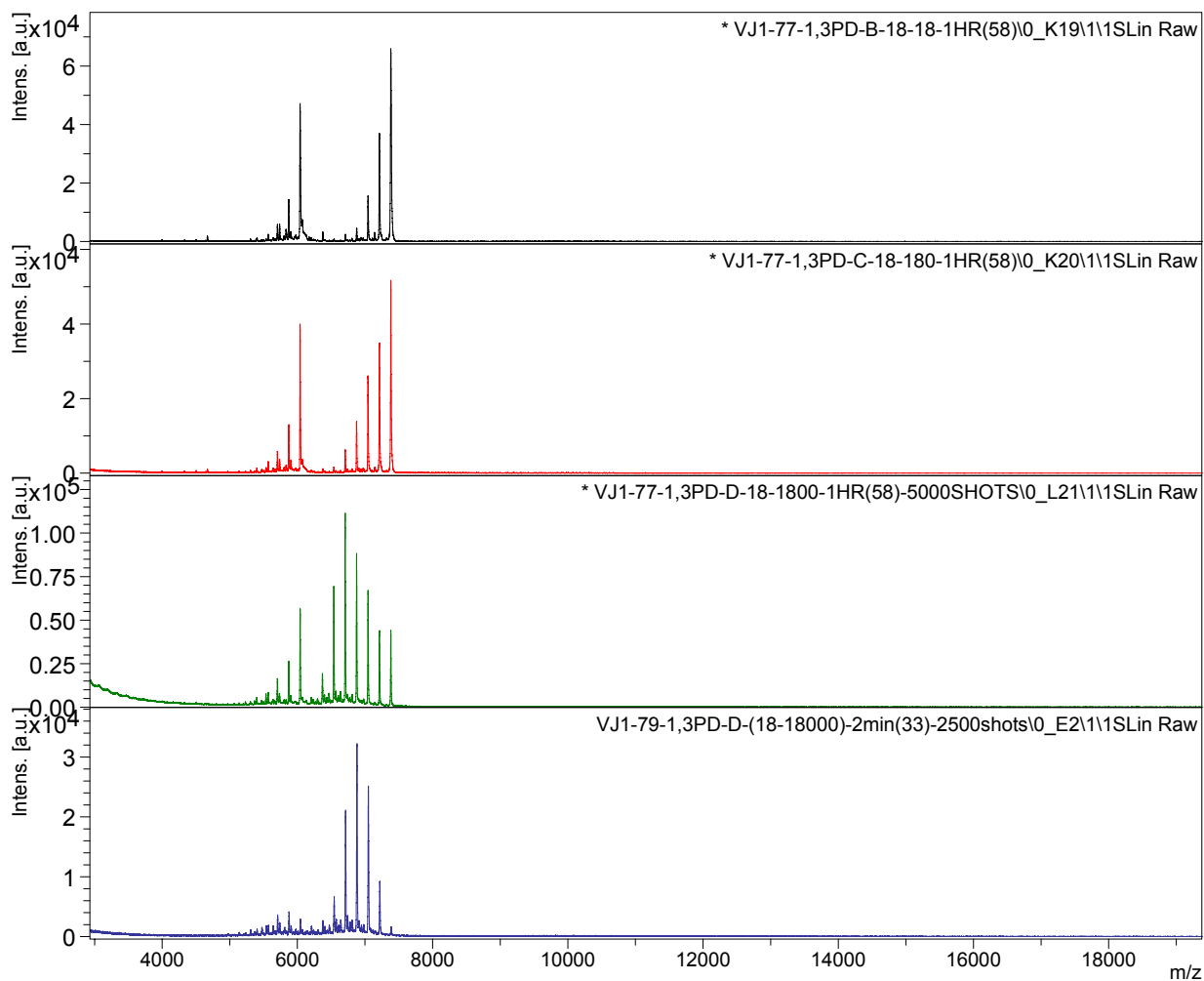
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Acquisition operation mode	Linear
Voltage polarity	POS
Number of shots	1000
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 13. MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,3-propanedithiol as a function of the ratio of starting nanocluster to dithiol. Figure 4 in the manuscript is extracted from this data.

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Acquisition Parameter

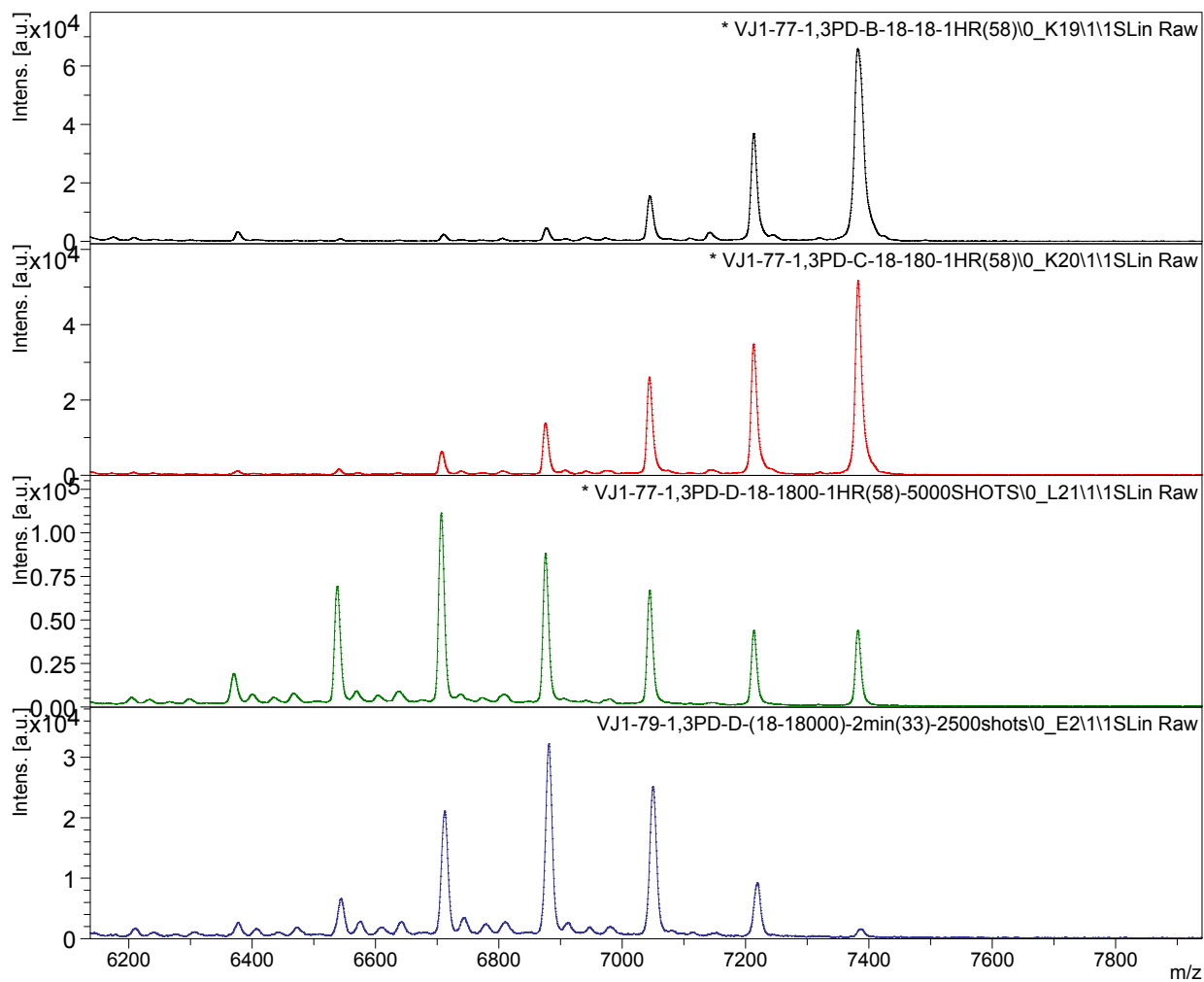
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Acquisition operation mode	Linear
Voltage polarity	POS
Number of shots	2500
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 14. Expanded MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,3-propanedithiol as a function of the ratio of starting nanocluster to dithiol. Figure 4 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\101018\VJ1-77-1,3PD-B-18-18\VJ1-77-1,3PD-B-18-18-1HR(58)\0_K19\1



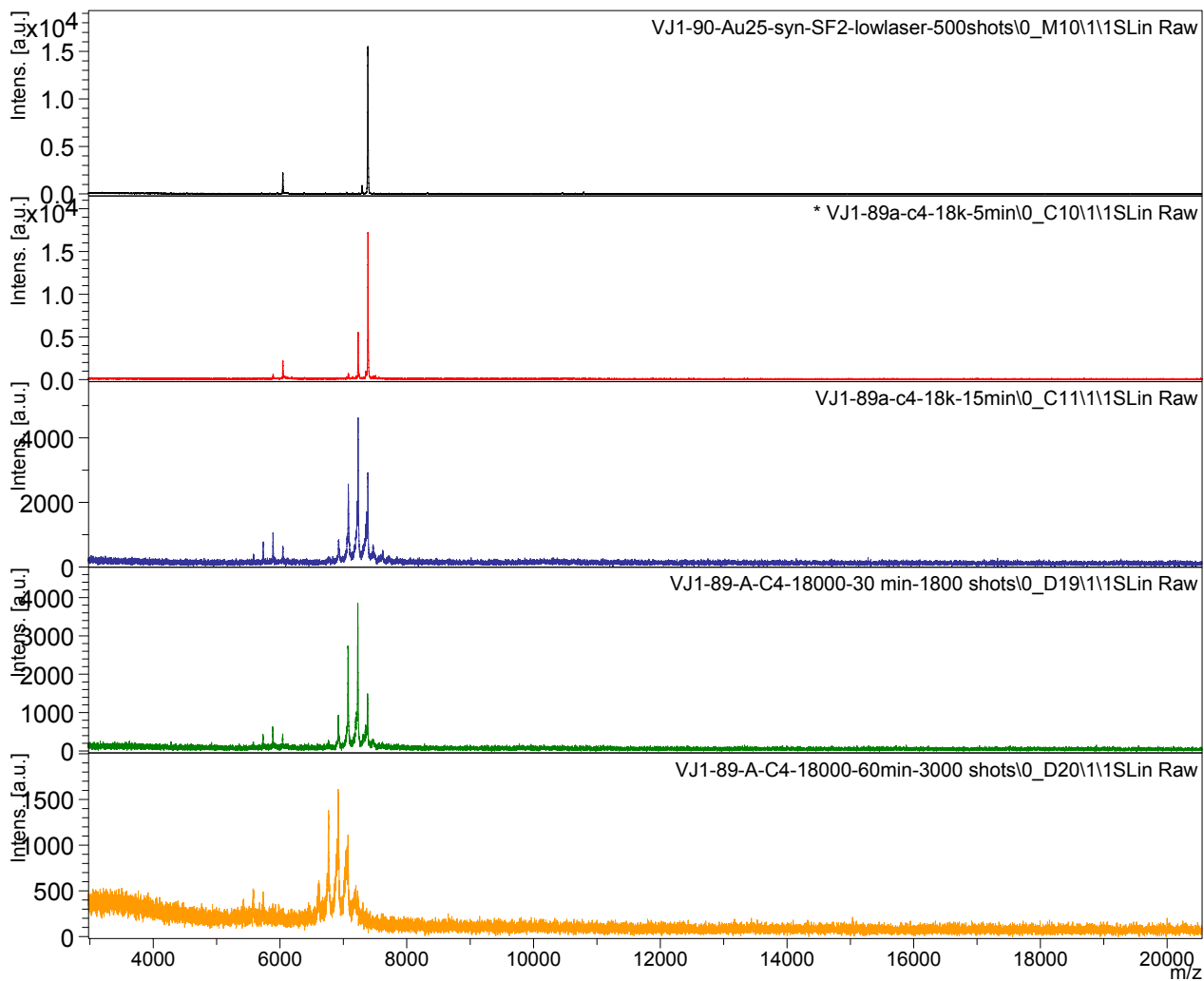
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Voltage polarity	POS
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Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 15. MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol as a function of time. Figure 5 in the manuscript is extracted from this data.



Acquisition Parameter

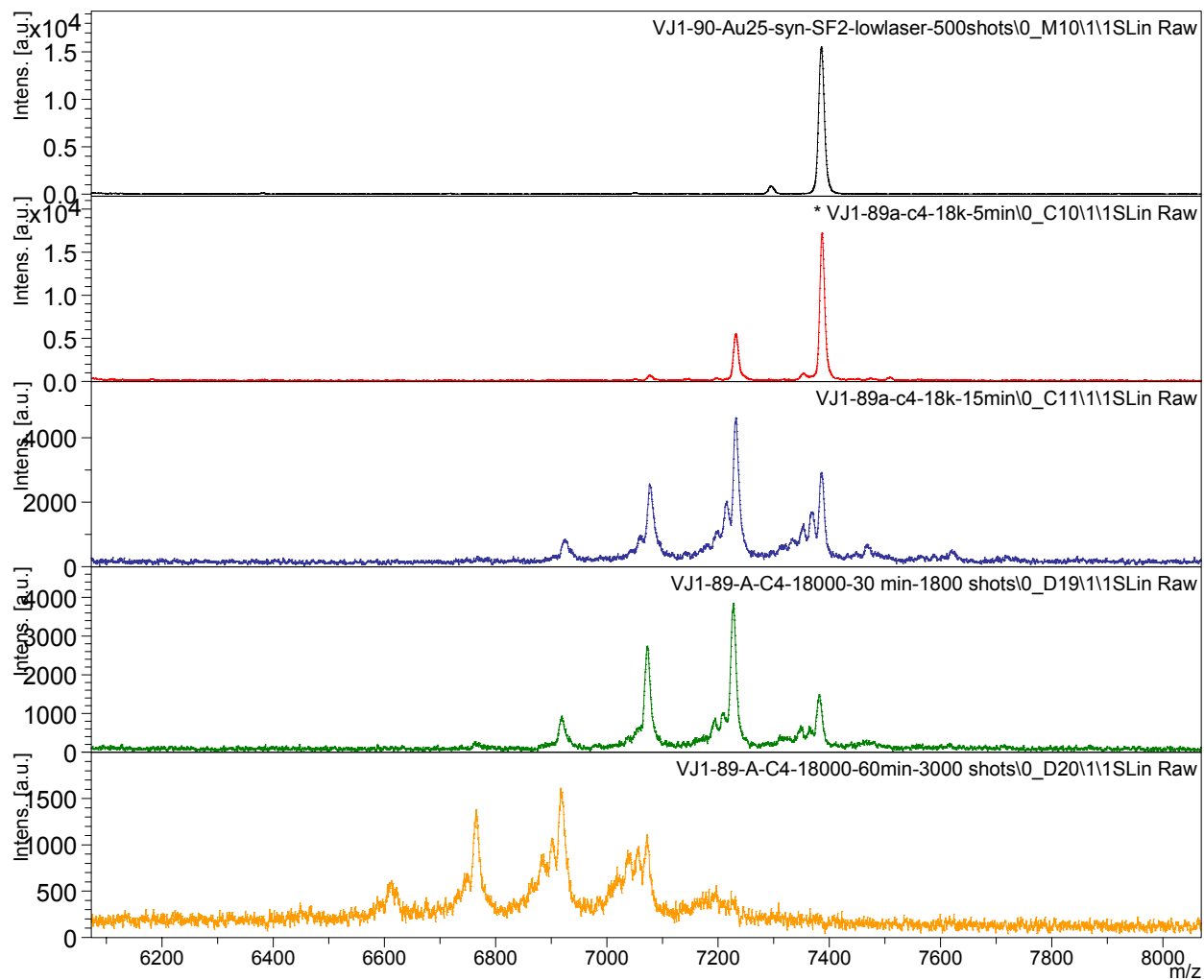
Date of acquisition
Acquisition method name
Acquisition mode
Acquisition operation mode
Voltage polarity
Number of shots
Name of spectrum used for calibration
Calibration reference list used

Instrument Info

Instrument type

Supporting Figure 16. Expanded MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol as a function of time. Figure 5 in the manuscript is extracted from this data.

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Acquisition Parameter

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Calibration reference list used	

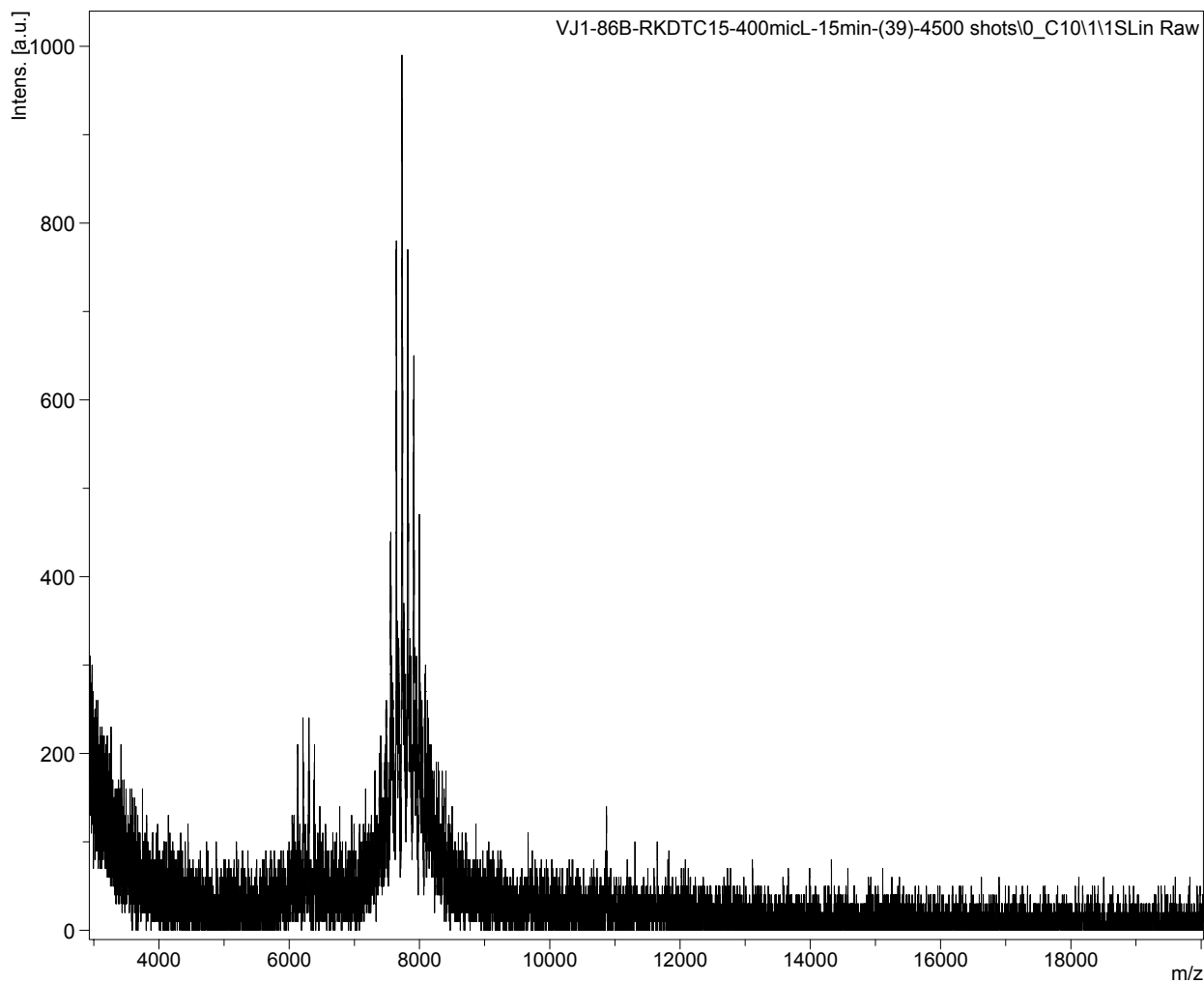
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Supporting Figure 17. MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with C15 analogue of 1,3-propanedithiol. Figure 10 in the manuscript is extracted from this data. The data shown in the manuscript is smoothed for better signal to noise ratio.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\101128\VJ1-86-B-RKDTC15(R3)\VJ1-86B-RKDTC15-400micL-15min-(39)-4500 shots\0_C10\1



Acquisition Parameter

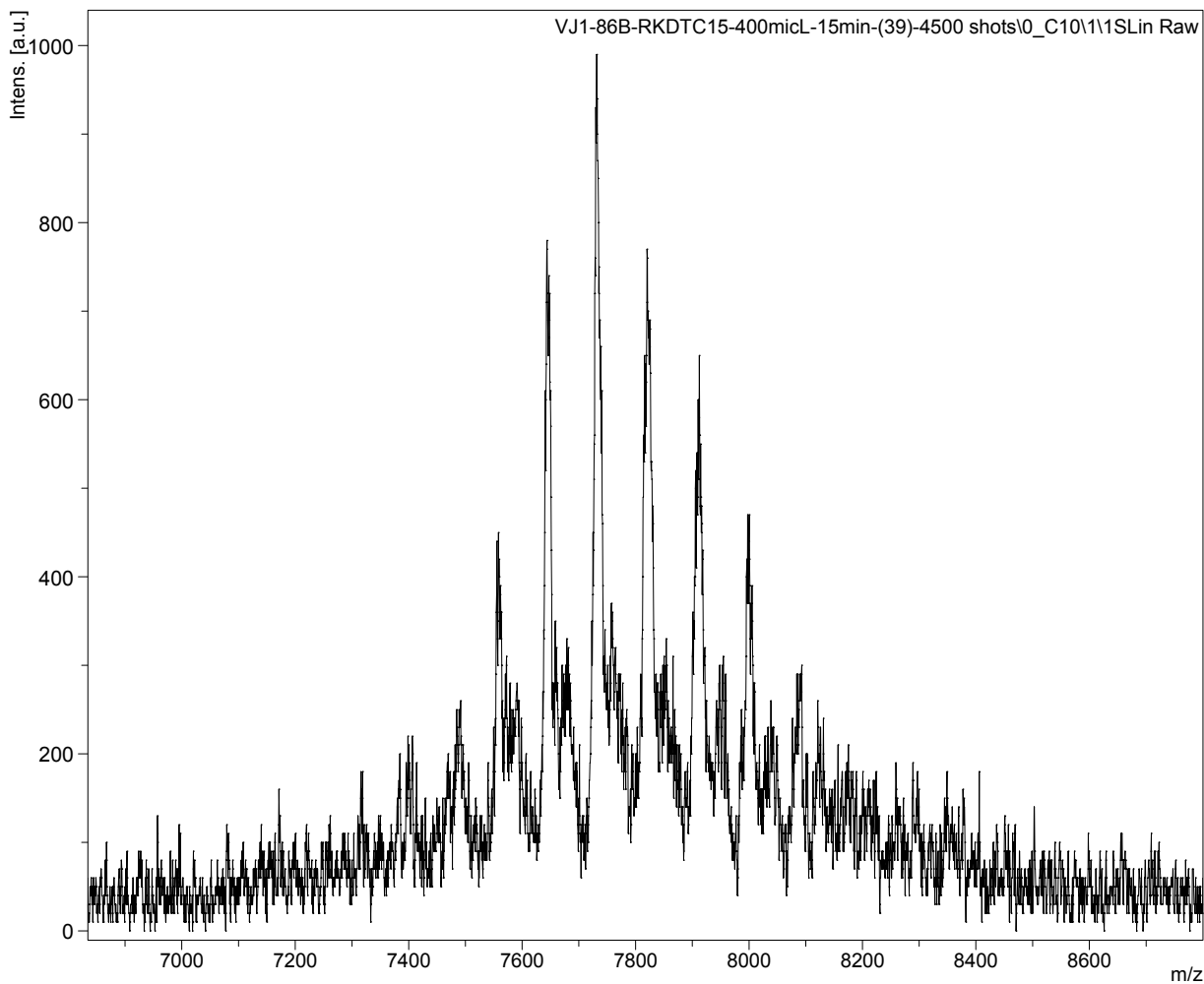
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Acquisition mode	qsim
Acquisition operation mode	Linear
Voltage polarity	POS
Number of shots	4500
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 18. Expanded MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with C15 analogue of 1,3-propanedithiol. Figure 10 in the manuscript is extracted from this data. The data shown in the manuscript is smoothed for better signal to noise ratio.

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Acquisition Parameter

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Acquisition operation mode	Linear
Voltage polarity	POS
Number of shots	4500
Name of spectrum used for calibration	
Calibration reference list used	

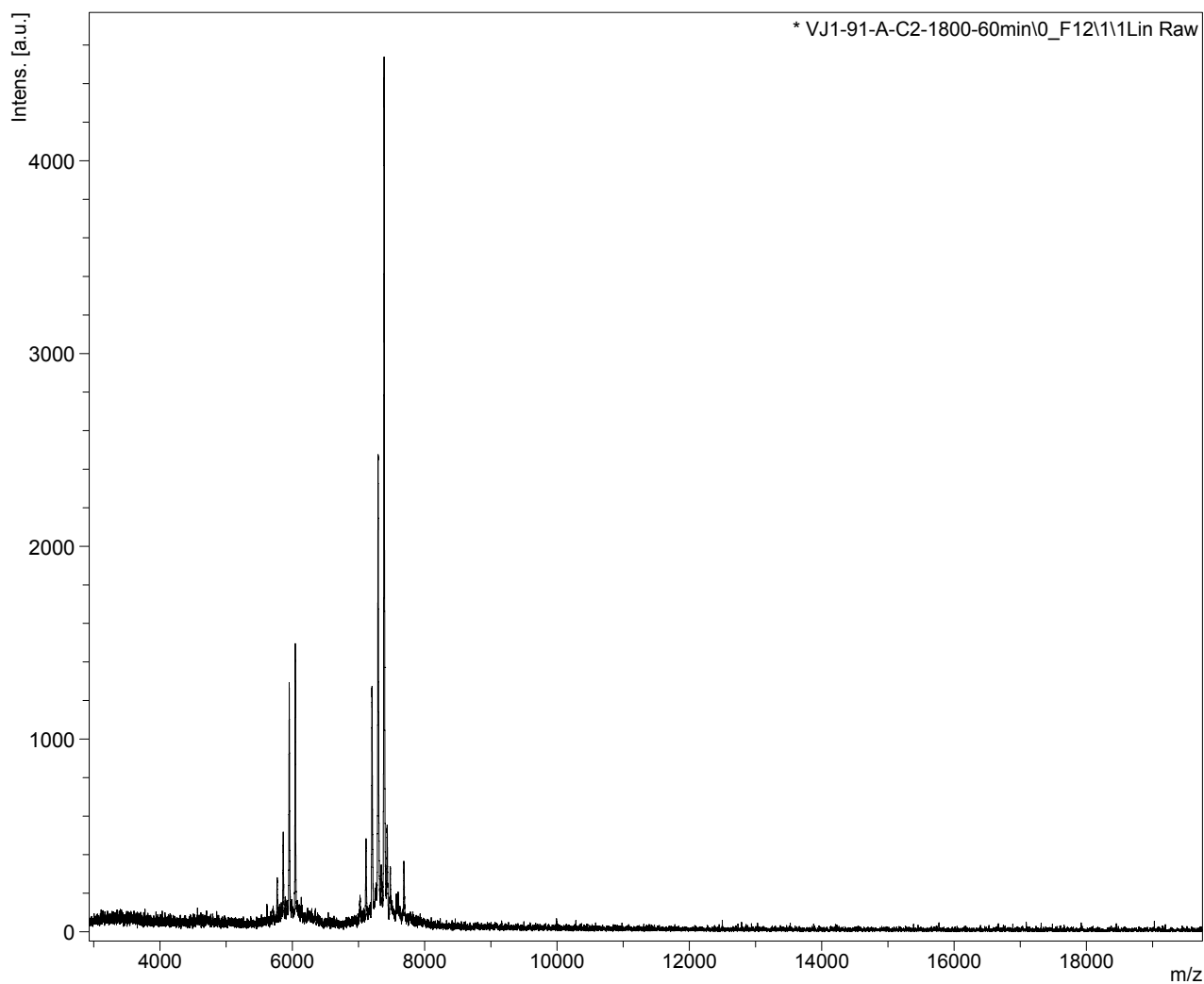
Instrument Info

Instrument type	autoflex
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Supporting Figure 19. MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,2-ethanedithiol. Figure 11 in the manuscript is extracted from this data.

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Acquisition Parameter

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Calibration reference list used	

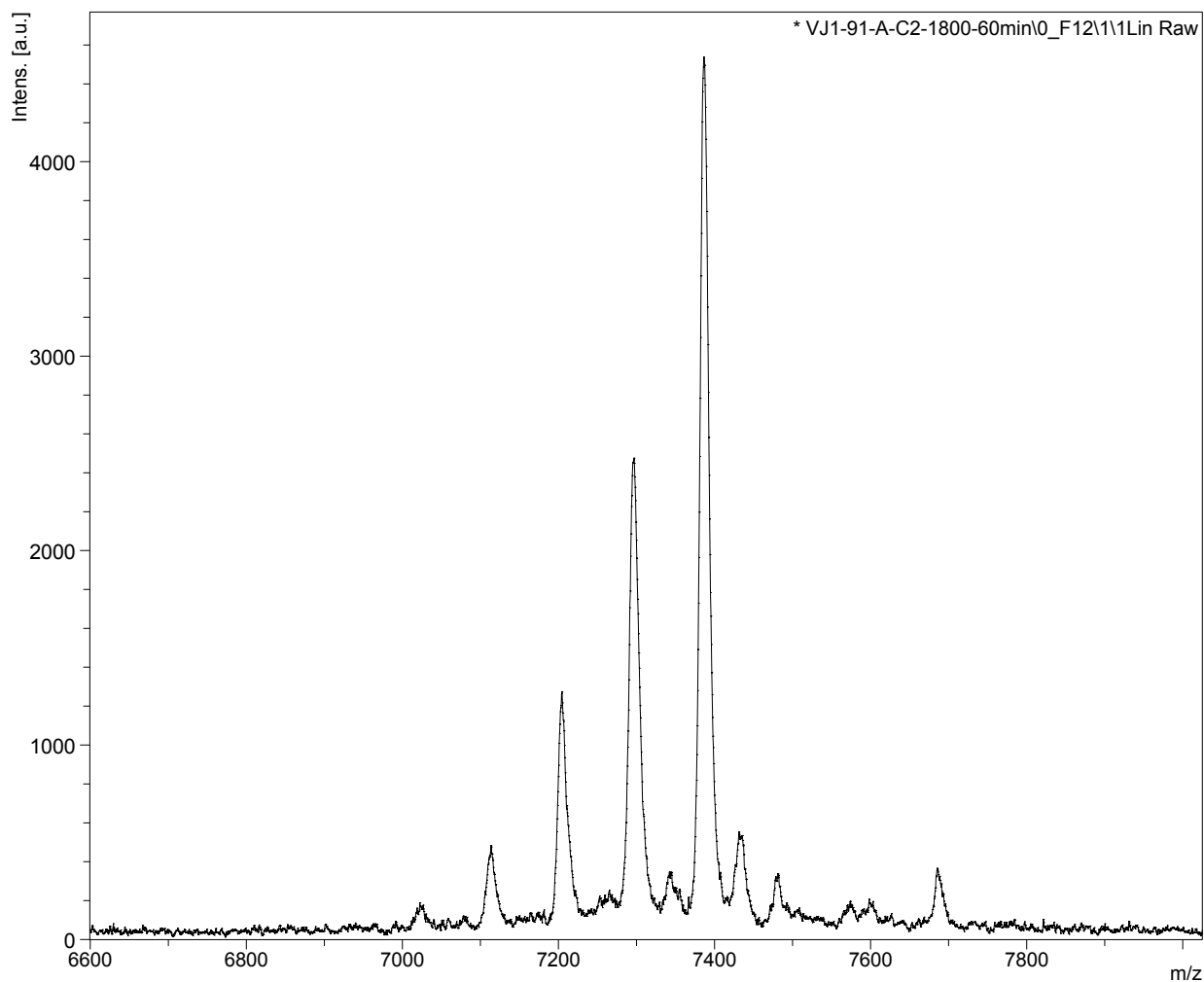
Instrument Info

Instrument type	autoflex
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Supporting Figure 20. Expanded MALDI spectrum of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$ ligand exchanged with 1,2-ethanedithiol. Figure 11 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\110112\VJ1-91-A-C2-1800-60min\0_F12\1



Acquisition Parameter

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Number of shots	500
Name of spectrum used for calibration	
Calibration reference list used	

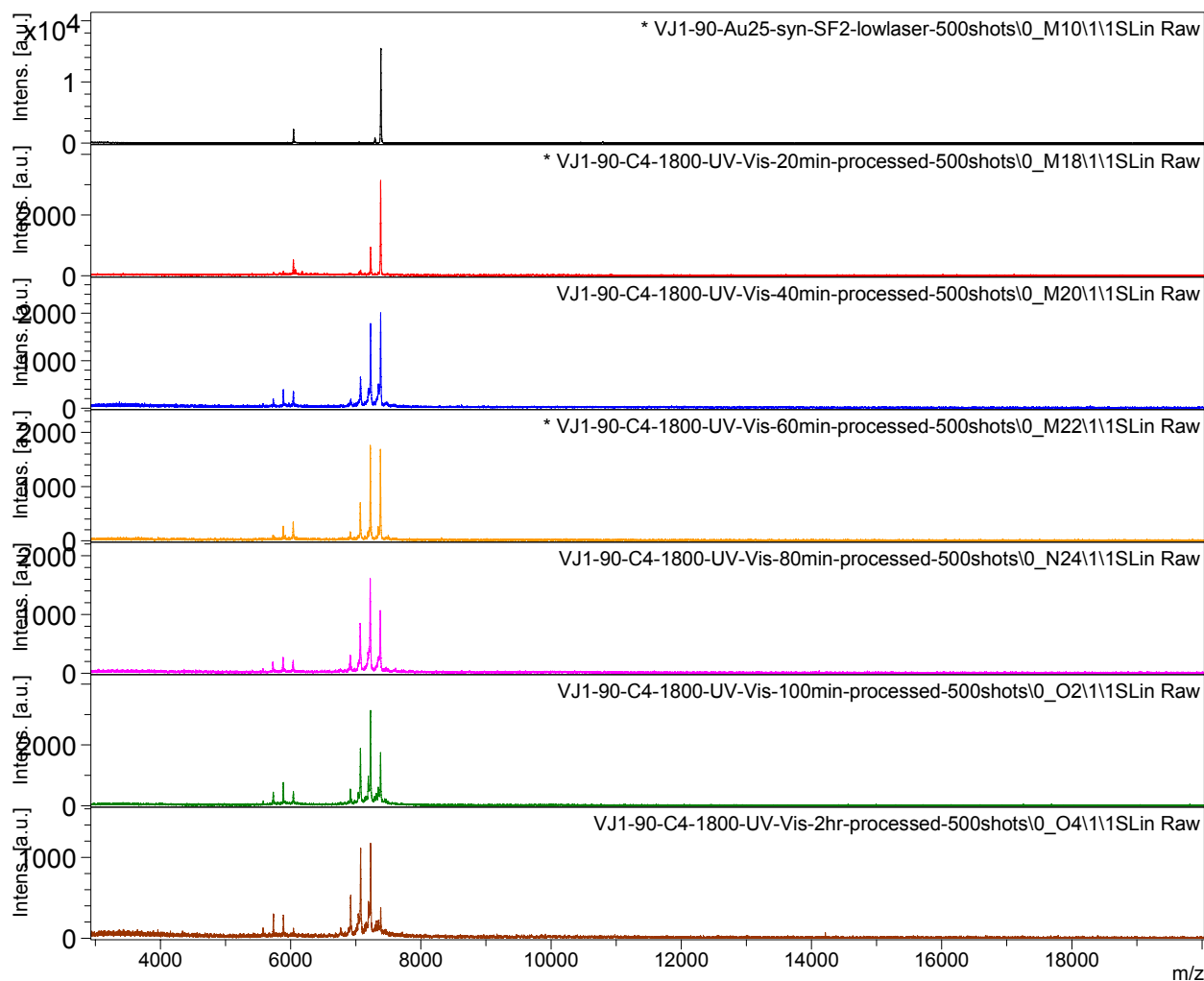
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Instrument type	autoflex
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Supporting Figure 21. MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{SCH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol as a function of reaction time. Same samples were used for the UV-vis measurements. Figure 13 in the manuscript is extracted from this data.

D:\Data\Vijay\VJ1-Fall-Spring-2010-11\110103\VJ1-90-B-C4-1800-LE-UV-Vis\VJ1-90-C4-1800-UV-Vis-2hr-processed-500shots\0_O4\1



Acquisition Parameter

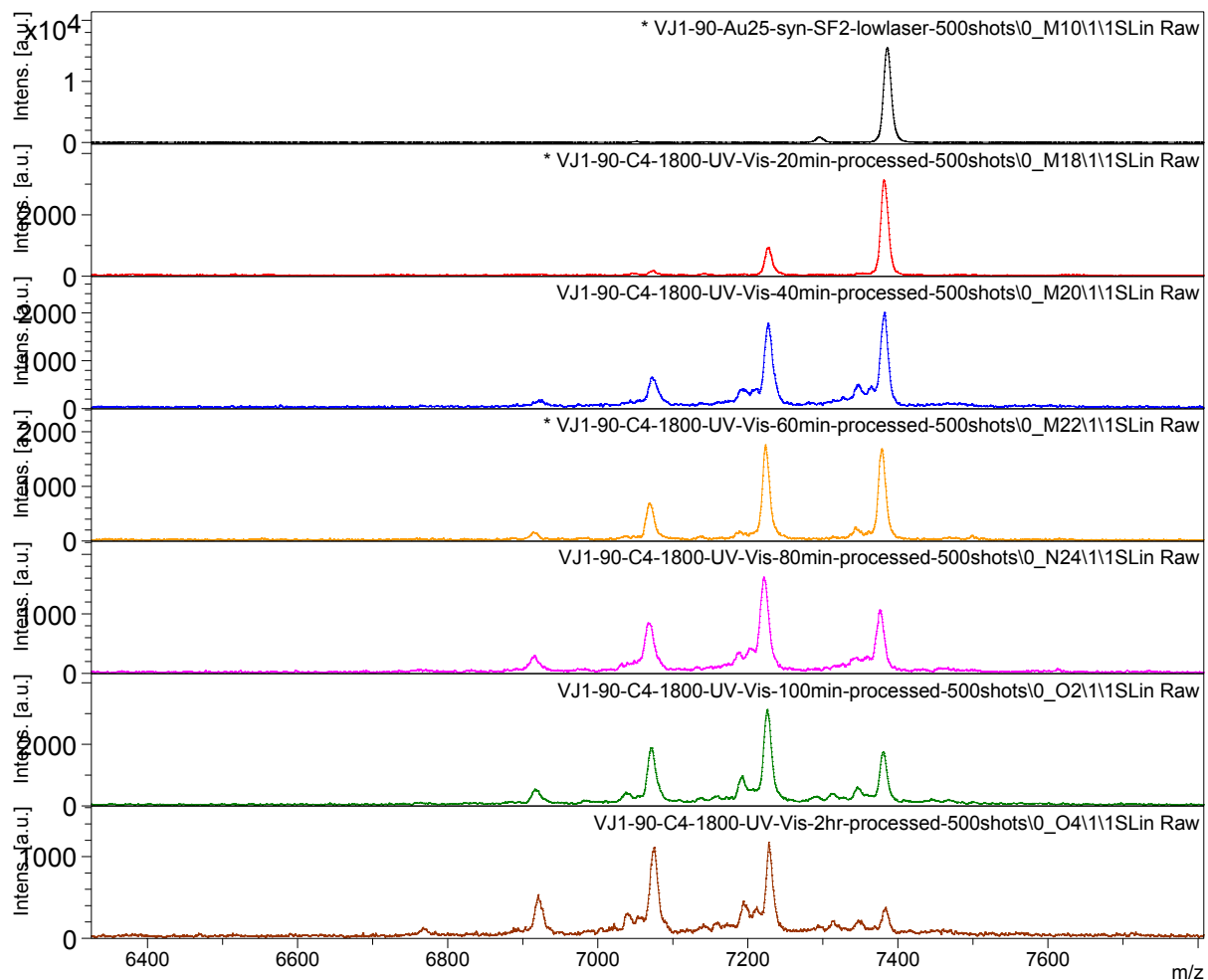
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Number of shots	500
Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Supporting Figure 22. Expanded MALDI spectra of $\text{Au}_{25}(\text{SCH}_2\text{SCH}_2\text{Ph})_{18}$ ligand exchanged with 1,4-butanedithiol as a function of reaction time. Same samples were used for the UV-vis measurements. Figure 13 in the manuscript is extracted from this data.

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Acquisition Parameter

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Name of spectrum used for calibration	
Calibration reference list used	

Instrument Info

Instrument type	autoflex
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Complete ref. 55 in main article

(55) Gaussian 09, R. A., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.