

Supporting Information

Top-Down Mass Analysis of Protein Tyrosine Nitration: Comparison of Electron Capture Dissociation with ‘Slow-Heating’ Tandem Mass Spectrometry Methods

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a

G L S D G E W Q Q V L N V W G K V E A D I A G H G Q E V L I
R L F T G H P E T L E K F D K F K H L K T E A E M K A S E D
L K K H G T V V L T A L G G I L K K K G H H E A E L K P L A
Q S H A T K H K L P L K Y L E F I S D A I I H V L H S K H P
G D F G A D A Q G A M T K A L E L F R N D I A A K Y K E L G
F Q G

b

G L S D G E W Q Q V L N V W G K V E A D I A G H G Q E V L I
R L F T G H P E T L E K F D K F K H L K T E A E M K A S E D
L K K H G T V V L T A L G G I L K K K G H H E A E L K P L A
Q S H A T K H K L P L K Y L E F I S D A I I H V L H S K H P
G D F G A D A Q G A M T K A L E L F R N D I A A K Y K E L G
F Q G

c

G L S D G E W Q Q V L N V W G K V E A D I A G H G Q E V L I
R L F T G H P E T L E K F D K F K H L K T E A E M K A S E D
L K K H G T V V L T A L G G I L K K K G H H E A E L K P L A
Q S H A T K H K L P L K Y L E F I S D A I I H V L H S K H P
G D F G A D A Q G A M T K A L E L F R N D I A A K Y K E L G
F Q G

Figure S-1. Summary of fragment ions from the 20+ ions of unmodified myoglobin: (a) *c'* and *z•* ECD fragments, (b) IRMPD and (c) CID *b* and *y* fragments.

a

K V F G|R)C E L)A)A)A)M)K)R H)G L)D N)Y)R G Y S L G N W V C
A A K F E S N F N T Q A T N R N T D G S T D Y G I L Q I N S
R W W C N D G R T P G S R N L C N I P C S A L L S S D I T A
S V N C A K K I V S D G N G M N A W V A W R N R C K G T D V
Q A W I R G C R L

b

K V F G|R)C E L)A)A)A)M)K)R H G L D N Y R G Y S L G N W V C
A A K F E S N F N T Q A T N R N T D G S T D Y G I L Q I N S
R W W C N D G R T P G S R N L C N I P C S A L L S S D I T A
S V N C A K K I V S D G N G M N A W V A W R N R C K G T D V
Q A W I R G C R L

c

K V F G|R)C E L)A)A)A)M)K)R H G L D N Y R G Y S L G N W V C
A A K F E S N F N T Q A T N R N T D G S T D Y G I L Q I N S
R W W C N D G R T P G S R N L C N I P C S A L L S S D I T A
S V N C A K K I V S D G N G M N A W V A W R N R C K G T D V
Q A W I R G C R L

Figure S-2. Summary of ECD fragments (c' and $z\bullet$ ions) from the 10+ ions of non-reduced (a) unmodified (b) mono- and (c) bis-nitrated lysozyme. Mass shift -1 Da is assumed for circled cysteine residues (see text in the main manuscript). Nitrated tyrosine residues are circled.

K V F G R C E L A A A M K R H G L D N Y R G S L G N W V C
 A A K F E S N F N T Q A T N R N T D G S T D Y G I L Q I N S
 R W W C N D G R T P G S R N L C N I P C S A L L S S D I T A
 S V N C A K K I V S D G N G M N A W V A W R N R C K G T D V
 Q A W I R G C R L

PScore: 8.849e-44

a

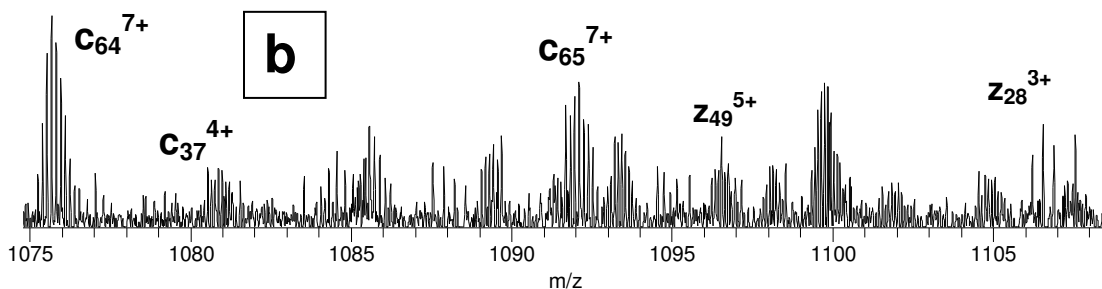
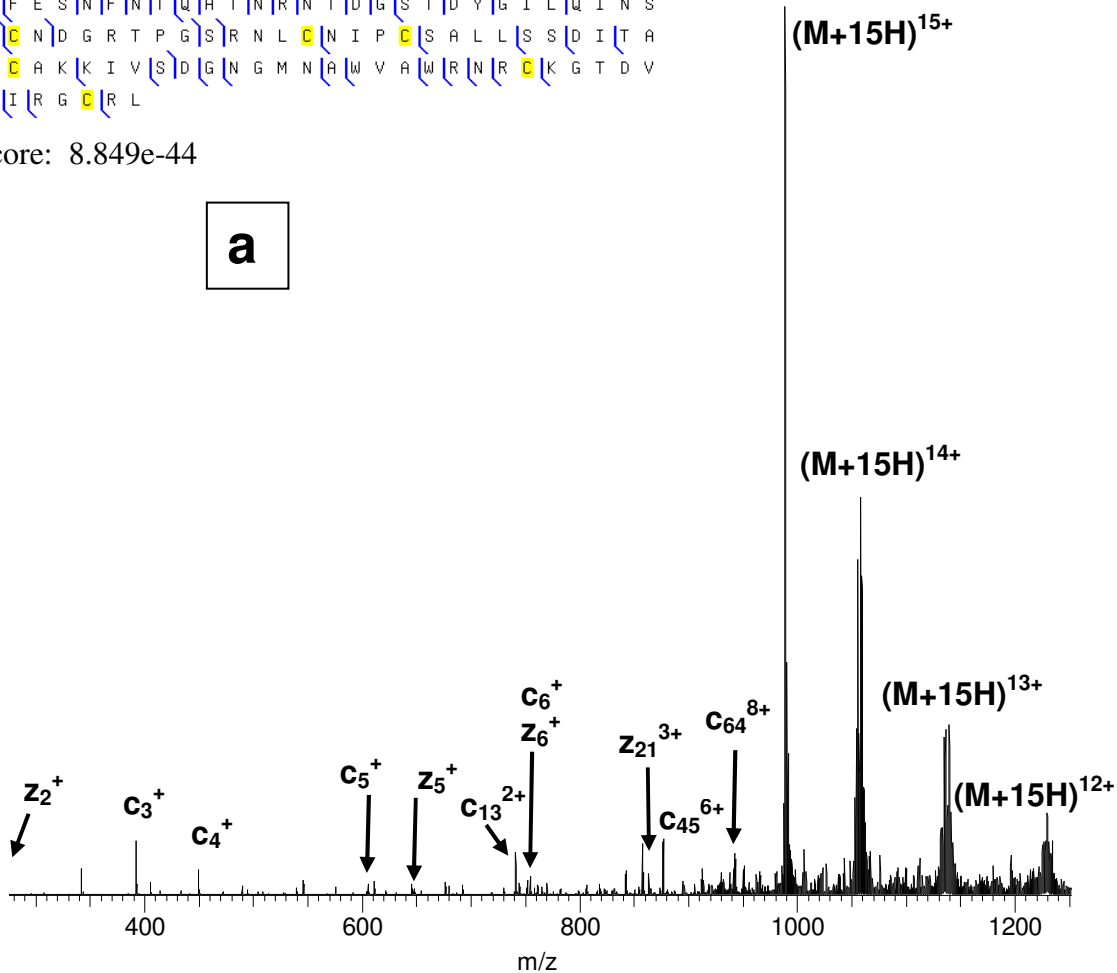


Figure S-3. ECD MS/MS spectra and fragment summary of the 15+ charge state of reduced mono-nitrated lysozyme (a) over the range of all m/z values where the fragments were found and (b) zoom-in between m/z = 1075 - 1108 with isotopic distributions of some of the fragments.

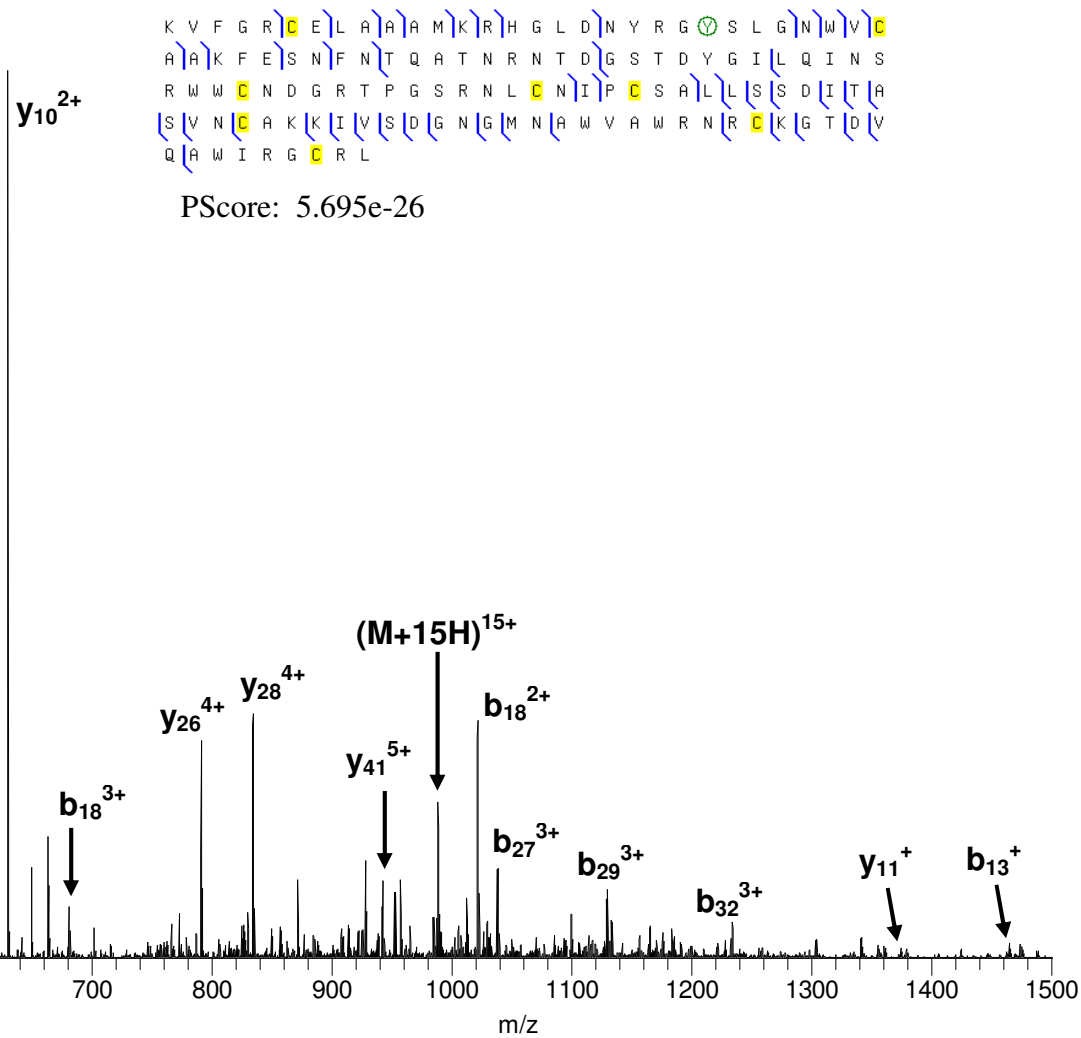


Figure S-4. IRMPD MS/MS spectra and fragment summary of the 15+ charge state of reduced mono-nitrated lysozyme.

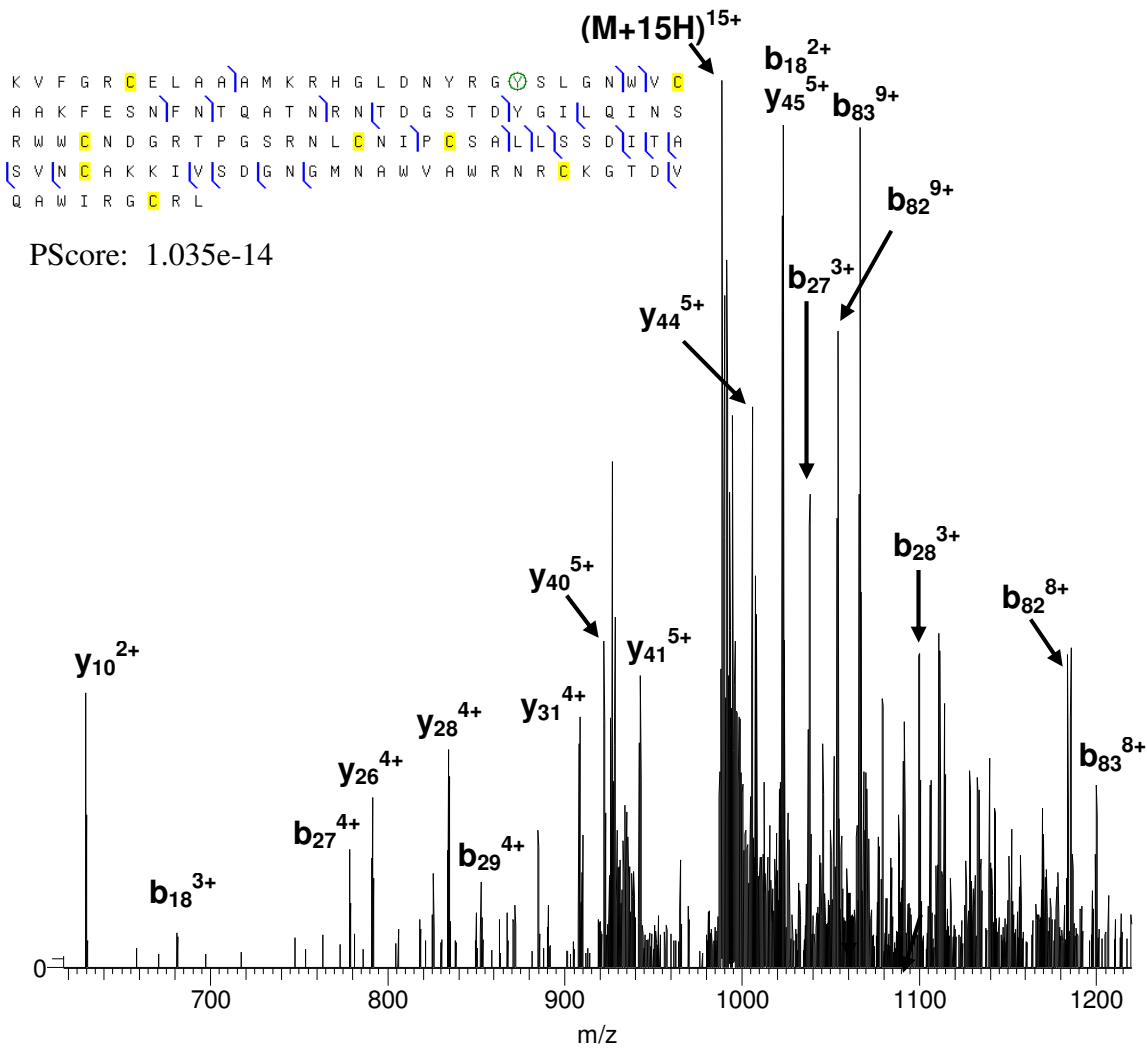


Figure S-5. CID MS/MS spectra and fragment summary of the 15+ charge state of reduced mono-nitrated lysozyme.