Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Relative Quantitation of Primary Amines and Sulfhydryl Groups Using Metal Chelation Tags

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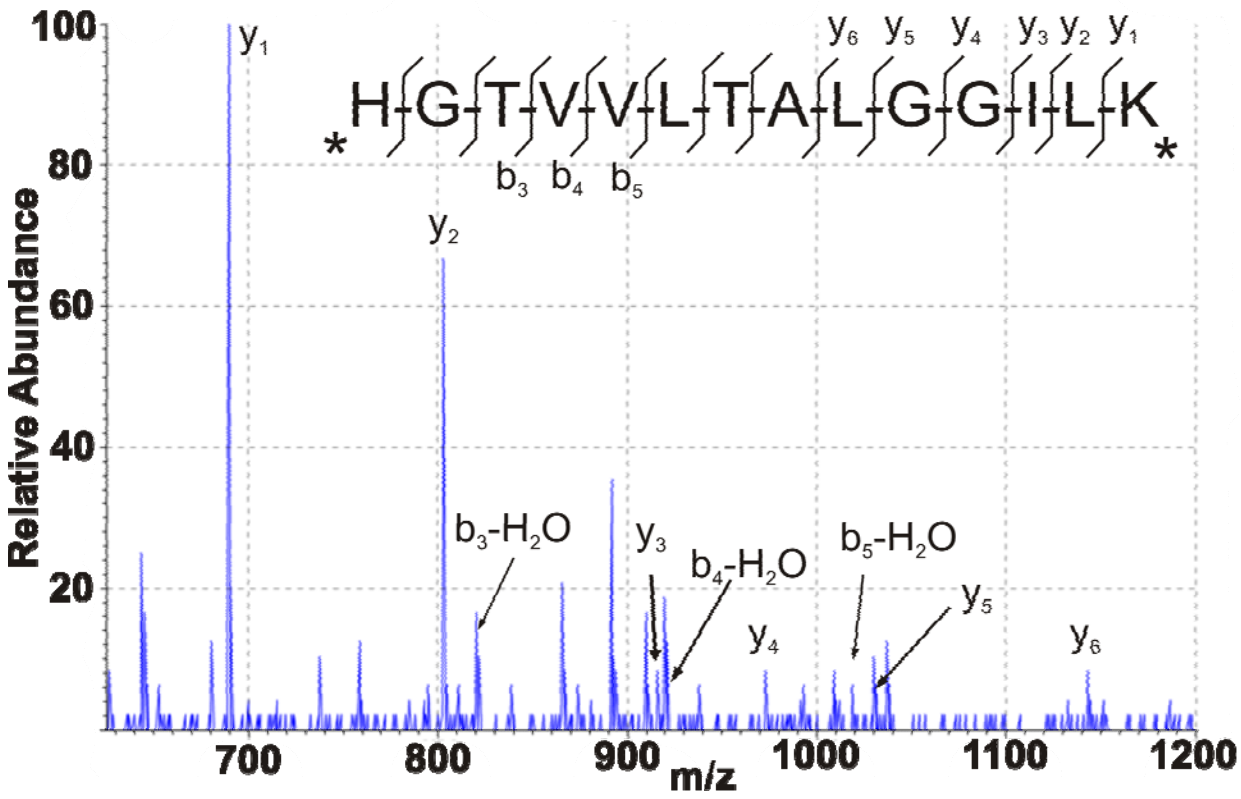
Abstract: Metal chelation tags, which can incorporate a variety of lanthanide metals, broaden the scope of possible relative quantitation measurements since the number of experimental conditions is limited only by the number of lanthanides used.



Peptide Fragment	y_1	y_2	y_3	y_4	y_5	y_6	b_3-H_2O	b_4-H_2O	b_5-H_2O
m/z	688.5	801.6	914.7	971.7	1028.7	1141.8	819.5	918.6	1017.7

Figure S1. Tandem MS spectrum (generated using a MALDI ion source) of a peptide (HGTVVLTALGGILK) from a myoglobin digest labeled with the primary amine specific shift reagent. The peptide sequence is shown above with an asterisk (*) marking the location of tag addition (i.e. at the N-terminus and the Lys residue). Labeled b and y ion peaks correspond to the fragment mass including the additional mass of the label since both termini are labeled.

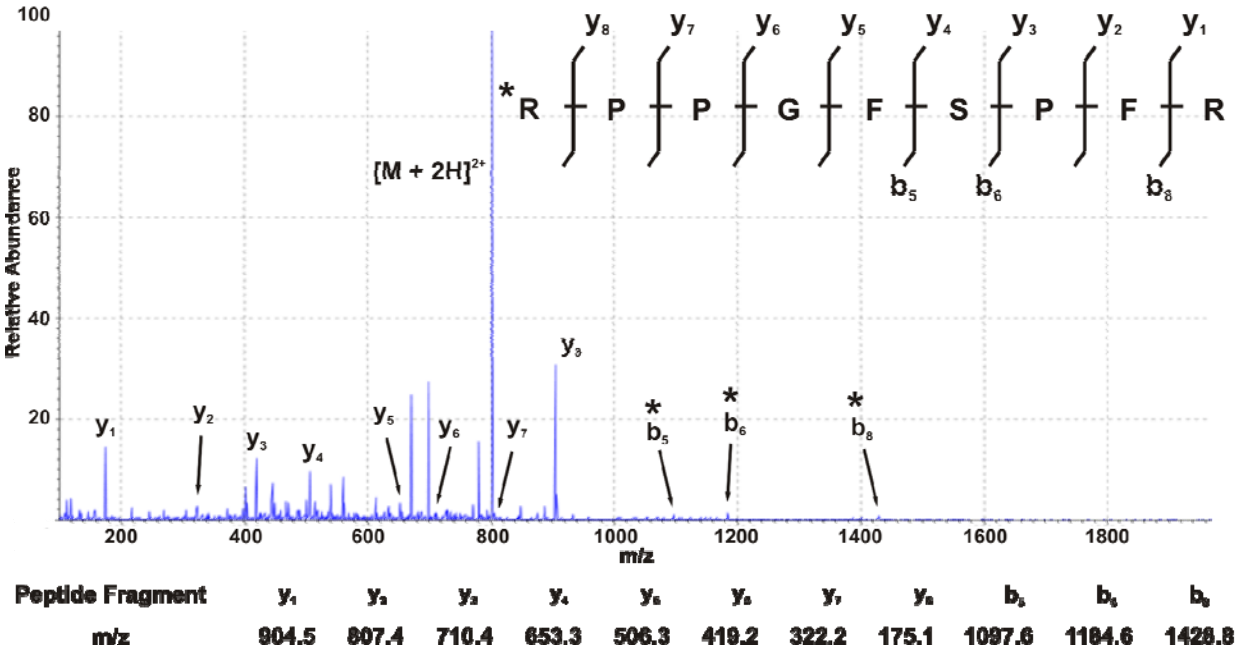


Figure S2. Tandem MS spectrum (generated using an ESI ion source) of bradykinin (RPPGFSPFR) labeled at the N-terminus with a terbium chelated primary amine specific label. The peptide sequence is shown above with an asterisk (*) indicating the location of tag addition. Labeled b and y ion peaks correspond to the fragment mass including the additional mass of the label. Peaks containing the Tb label are indicated with an asterisk.

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
136	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-
138	0.1	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-
139	99.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
140	-	88.5	-	-	-	-	-	-	-	-	-	-	-	-	-
141	-	tr	100	-	-	-	-	-	-	-	-	-	-	-	-
142	-	11.1	-	27.2	-	-	-	-	-	-	-	-	-	-	-
143	-	-	-	12.2	-	-	-	-	-	-	-	-	-	-	-
144	-	tr	-	23.8	-	3.1	-	-	-	-	-	-	-	-	-
145	-	-	-	8.3	-	-	-	-	-	-	-	-	-	-	-
146	-	-	-	17.2	-	-	-	-	-	-	-	-	-	-	-
147	-	-	-	-	-	15.0	-	-	-	-	-	-	-	-	-
148	-	-	-	5.7	-	11.2	-	-	-	-	-	-	-	-	-
149	-	-	-	-	-	13.9	-	-	-	-	-	-	-	-	-
150	-	-	-	5.6	-	7.4	-	-	-	-	-	-	-	-	-
151	-	-	-	-	-	-	47.8	-	-	-	-	-	-	-	-
152	-	-	-	-	-	26.8	-	0.2	-	-	-	-	-	-	-
153	-	-	-	-	-	-	52.2	-	-	-	-	-	-	-	-
154	-	-	-	-	-	22.8	-	2.2	-	-	-	-	-	-	-
155	-	-	-	-	-	-	-	14.8	-	-	-	-	-	-	-
156	-	-	-	-	-	-	-	20.5	-	tr	-	-	-	-	-
157	-	-	-	-	-	-	-	15.7	-	-	-	-	-	-	-
158	-	-	-	-	-	-	-	24.8	-	0.1	-	-	-	-	-
159	-	-	-	-	-	-	-	-	100	-	-	-	-	-	-
160	-	-	-	-	-	-	-	21.9	-	2.3	-	-	-	-	-
161	-	-	-	-	-	-	-	-	-	18.9	-	-	-	-	-
162	-	-	-	-	-	-	-	-	-	25.5	-	0.1	-	-	-
163	-	-	-	-	-	-	-	-	-	24.9	-	-	-	-	-
164	-	-	-	-	-	-	-	-	-	28.3	-	1.6	-	-	-
165	-	-	-	-	-	-	-	-	-	-	100	-	-	-	-
166	-	-	-	-	-	-	-	-	-	-	-	33.5	-	-	-
167	-	-	-	-	-	-	-	-	-	-	-	22.9	-	-	-
168	-	-	-	-	-	-	-	-	-	-	-	27.0	-	0.1	-
169	-	-	-	-	-	-	-	-	-	-	-	-	100	tr	-
170	-	-	-	-	-	-	-	-	-	-	-	14.9	-	3.0	-
171	-	-	-	-	-	-	-	-	-	-	-	-	-	14.3	-
172	-	-	-	-	-	-	-	-	-	-	-	-	-	21.8	-
173	-	-	-	-	-	-	-	-	-	-	-	-	-	16.1	-
174	-	-	-	-	-	-	-	-	-	-	-	-	-	31.8	-
175	-	-	-	-	-	-	-	-	-	-	-	-	-	-	97.4
176	-	-	-	-	-	-	-	-	-	-	-	-	-	12.8	2.6

Table ST1. Table of lanthanide isotopes and relative abundance values useful for selection of the metal for incorporation in the tag.

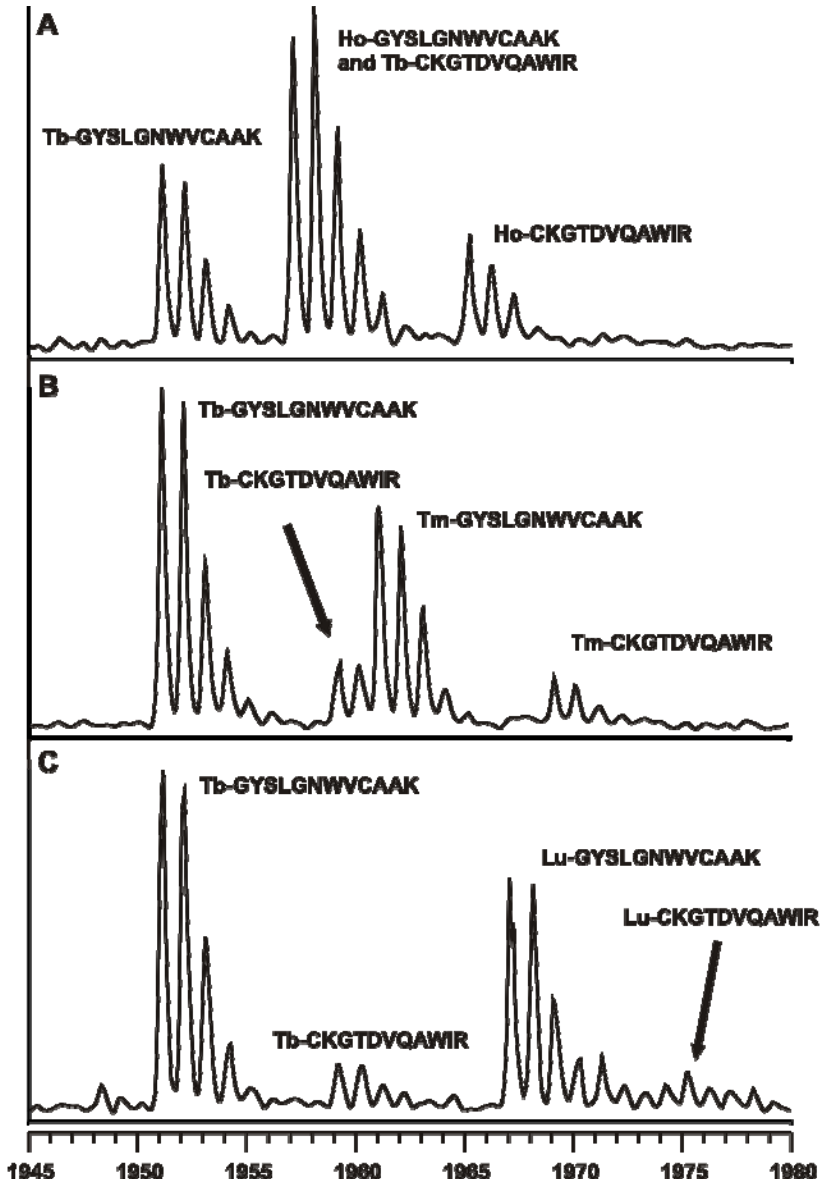
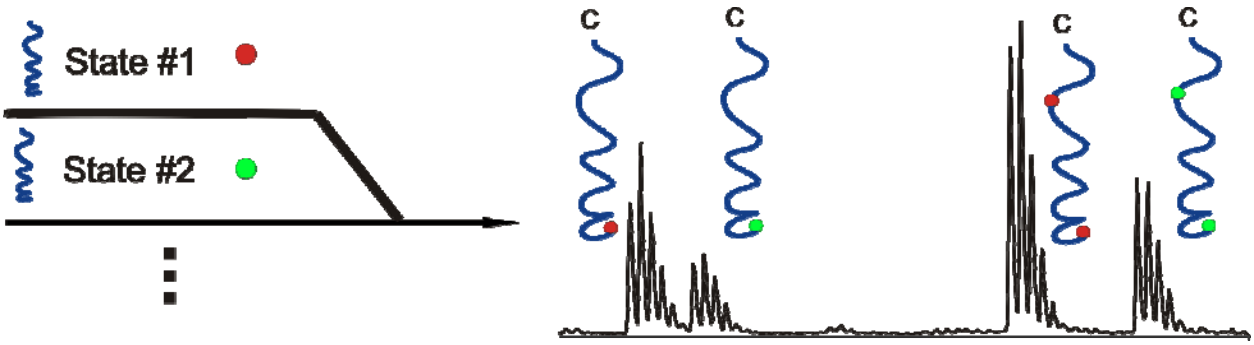


Figure S3. Spectra illustrating the importance and possiblities of lanthanide metal selection. Chicken egg white lysozyme was digested using trypsin and then tagged using Ho/Tb (A), Tm/Tb (B), and Lu/Tb, (C). Since two peaks overlapped in spectrum A, the metal system was changed which resulted in better resolution of peaks in spectrum B. Spectrum C shows that the peaks were fully resolved using the Lu/Tb metal system.


State #1
State #2
C
C
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