Electronic Supplementary Information

Matrix-Assisted Nanoelectrospray Mass Spectrometry for Soft Ionization of Metal(I)-Protein Complexes

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Table S1. Comparison of the difference in mass-to-charge ratios between theoretical values and experimental data using a TSQ mass spectrometer after the interaction of $Cu(NO_3)_2$ and myoglobin.

charge	m/z (exper.)	Cu(I)			Cu(II)		
		formula	m/z (theor.)	Δm	formula	m/z (theor.)	Δm
14+	1215.83	$[M+Cu^{I}+13H]^{14+}$	1215.83	0.00	$[M+Cu^{II}+12H]^{14+}$	1215.76	-0.07
	1220.15	$[M+2Cu^{I}+12H]^{14+}$	1220.26	0.11	$[M+2Cu^{II}+10H]^{14+}$	1220.11	-0.04
	1224.54	$[M+3Cu^{I}+11H]^{14+}$	1224.68	0.14	$[M+3Cu^{II}+8H]^{14+}$	1224.47	-0.07
	1229.38	$[M+4Cu^{I}+10H]^{14+}$	1229.11	-0.27	$[M+4Cu^{II}+6H]^{14+}$	1228.82	0.56
15+	1134.78	$[M+Cu^{I}+14H]^{15+}$	1134.84	0.06	$[M+Cu^{II}+13H]^{15+}$	1134.77	-0.01
	1138.83	$[M+2Cu^{I}+13H]^{15+}$	1138.97	0.15	$[M+2Cu^{II}+11H]^{15+}$	1138.84	0.01
	1142.88	$[M+3Cu^{I}+12H]^{15+}$	1143.11	0.22	$[M+3Cu^{II}+9H]^{15+}$	1142.90	0.02
	1146.75	$[M+4Cu^{I}+11H]^{15+}$	1147.24	0.49	$[M+4Cu^{II}+7H]^{15+}$	1146.97	0.22
16+	1063.93	$[M+Cu^{I}+15H]^{16+}$	1063.98	0.05	$[M+Cu^{II}+14H]^{16+}$	1063.91	-0.02
	1067.76	$[M+2Cu^{I}+14H]^{16+}$	1067.85	0.09	$[M+2Cu^{II}+12H]^{16+}$	1067.72	-0.03
	1071.61	$[M+3Cu^{I}+13H]^{16+}$	1071.73	0.12	$[M+3Cu^{II}+10H]^{16+}$	1071.54	-0.07
	1075.30	$[M+4Cu^{I}+12H]^{16+}$	1075.60	0.30	$[M+4Cu^{II}+8H]^{16+}$	1075.35	0.04
17+	1001.34	$[M+Cu^{I}+16H]^{17+}$	1001.45	0.11	$[M+Cu^{II}+15H]^{17+}$	1001.39	0.05
	1004.94	$[M+2Cu^{I}+15H]^{17+}$	1005.10	0.15	$[M+2Cu^{II}+13H]^{17+}$	1004.98	0.03
	1008.64	$[M+3Cu^{I}+14H]^{17+}$	1008.74	0.11	$[M+3Cu^{II}+11H]^{17+}$	1008.56	-0.07
	1012.22	$[M+4Cu^{I}+13H]^{17+}$	1012.39	0.17	$[M+4Cu^{II}+9H]^{17+}$	1012.15	-0.07
18+	945.80	$[M+Cu^{I}+17H]^{18+}$	945.87	0.07	$[M+Cu^{II}+16H]^{18+}$	945.81	0.02
	949.17	$[M+2Cu^{I}+16H]^{18+}$	949.31	0.14	$[M+2Cu^{II}+14H]^{18+}$	949.20	0.03
	952.52	$[M+3Cu^{I}+15H]^{18+}$	952.76	0.24	$[M+3Cu^{II}+12H]^{18+}$	952.59	0.07
	955.98	$[M+4Cu^{I}+14H]^{18+}$	956.20	0.22	$[M+4Cu^{II}+10H]^{18+}$	955.98	0.00
19+	896.03	$[M+Cu^{I}+18H]^{19+}$	896.14	0.11	$[M+Cu^{II}+17H]^{19+}$	896.09	0.05
	899.23	$[M+2Cu^{I}+17H]^{19+}$	899.40	0.17	$[M+2Cu^{II}+15H]^{19+}$	899.30	0.07
	902.41	$[M+3Cu^{I}+16H]^{19+}$	902.66	0.25	$[M+3Cu^{II}+13H]^{19+}$	902.51	0.09
	905.74	$[M+4Cu^{I}+15H]^{19+}$	905.93	0.19	$[M+4Cu^{II}+11H]^{19+}$	905.72	-0.03
20+	851.28	$[M+Cu^{I}+19H]^{20+}$	851.38	0.10	$[M+Cu^{II}+18H]^{20+}$	851.33	0.05
	854.32	$[M+2Cu^{I}+18H]^{20+}$	854.48	0.16	$[M+2Cu^{II}+16H]^{20+}$	854.38	0.06
	857.40	$[M+3Cu^{I}+17H]^{20+}$	857.58	0.18	$[M+3Cu^{II}+14H]^{20+}$	857.43	0.03
	860.42	$[M+4Cu^{I}+16H]^{20+}$	860.68	0.27	$[M+4Cu^{II}+12H]^{20+}$	860.48	0.06
21+	810.79	$[M+Cu^{I}+20H]^{21+}$	810.89	0.10	$[M+Cu^{II}+19H]^{21+}$	810.84	0.05
	813.71	$[M+2Cu^{I}+19H]^{21+}$	813.84	0.13	$[M+2Cu^{II}+17H]^{21+}$	813.74	0.04
	816.70	$[M+3Cu^{I}+18H]^{21+}$	816.79	0.09	$[M+3Cu^{II}+15H]^{21+}$	816.65	-0.06
	819.62	$[M+4Cu^{I}+17H]^{21+}$	819.74	0.13	$[M+4Cu^{II}+13H]^{21+}$	819.55	-0.06
22+	773.97	$[M+Cu^{I}+21H]^{22+}$	774.08	0.10	$[M+Cu^{II}+20H]^{22+}$	774.03	0.06
	776.73	$[M+2Cu^{I}+20H]^{22+}$	776.89	0.16	$[M+2Cu^{II}+18H]^{22+}$	776.80	0.07
	779.55	$[M+3Cu^{I}+19H]^{22+}$	779.71	0.16	$[M+3Cu^{II}+16H]^{22+}$	779.57	0.02
23+	740.37	$[M+Cu^{I}+22H]^{23+}$	740.46	0.09	$[M+Cu^{II}+21H]^{23+}$	740.42	0.05
	742.96	$[M+2Cu^{I}+21H]^{23+}$	743.16	0.20	$[M+2Cu^{II}+19H]^{23+}$	743.07	0.11
	745.72	$[M+3Cu^{I}+20H]^{23+}$	745.85	0.14	$[M+3Cu^{II}+17H]^{23+}$	745.72	0.01

Table S2. Comparison of the difference in mass-to-charge ratios between theoretical values and experimental data using an Orbitrap mass spectrometer after the interaction of $Cu(NO_3)_2$ and myoglobin.

charge	m/z (exper.)	formula	m/z (theor.)	Δm
14+	1211.8012	$[M+14H]^{14+}$		
	1216.2247	$[M+Cu^{I}+13H]^{14+}$	1216.2241	0.0006
	1220.6477	$[M+2Cu^{I}+12H]^{14+}$	1220.6471	0.0006
	1225.0700	$[M+3Cu^{I}+11H]^{14+}$	1225.0701	-0.0001
	1229.4924	$[M+4Cu^{I}+10H]^{14+}$	1229.4931	-0.0007
15+	1131.0816	$[M+15H]^{15+}$		
	1135.2098	$[M+Cu^{I}+14H]^{15+}$	1135.2097	0.0001
	1139.3385	$[M+2Cu^{I}+13H]^{15+}$	1139.3379	0.0006
	1143.4653	$[M+3Cu^{I}+12H]^{15+}$	1143.4660	-0.0007
	1147.5948	$[M+4Cu^{I}+11H]^{15+}$	1147.5941	0.0007
16+	1060.4520	$[M+16H]^{16+}$		
	1064.3220	$[M+Cu^{I}+15H]^{16+}$	1064.3221	-0.0001
	1068.1297	$[M+Cu^{II}+Cu^{I}+13H]^{16+}$	1068.1293	0.0005
	1072.0630	$[M+3Cu^{I}+13H]^{16+}$	1072.0624	0.0006
	1075.9333	$[M+4Cu^{I}+12H]^{16+}$	1075.9325	0.0008
17+	998.1315	$[M+17H]^{17+}$		
	1001.7740	$[M+Cu^{I}+16H]^{17+}$	1001.7740	0.0000
	1005.4164	$[M+2Cu^{I}+15H]^{17+}$	1005.4164	0.0000
	1009.0004	$[M+Cu^{II}+2Cu^{I}+13H]^{17+}$	1008.9996	0.0008
	1012.7016	$[M+4Cu^{I}+13H]^{17+}$	1012.7014	0.0002
18+	942.7357	$[M+18H]^{18+}$		
	946.1201	$[M+Cu^{II}+16H]^{18+}$	946.1198	0.0003
	949.5599	$[M+Cu^{II}+Cu^{I}+15H]^{18+}$	949.5599	0.0000
	953.0005	$[M+Cu^{II}+2Cu^{I}+14H]^{18+}$	953.0000	0.0005
	956.4406	$[M+Cu^{II}+3Cu^{I}+13H]^{18+}$	956.4401	0.0007
19+	893.1712	$[M+19H]^{19+}$		
	896.4302	$[M+Cu^{I}+18H]^{19+}$	896.4303	-0.0001
	899.6362	$[M+Cu^{II}+Cu^{I}+16H]^{19+}$	899.6363	-0.0001
	902.9484	$[M+3Cu^{I}+16H]^{19+}$	902.9484	0.0000
	906.2083	$[M+4Cu^{I}+15H]^{19+}$	906.2074	0.0009
20+	848.5631	$[M+20H]^{20+}$		
	851.6590	$[M+Cu^{I}+19H]^{20+}$	851.6591	-0.0001
	854.7549	$[M+2Cu^{I}+18H]^{20+}$	854.7552	-0.0003
	857.8515	$[M+3Cu^{I}+17H]^{20+}$	857.8513	0.0002
	860.8983	$[M+Cu^{II}+3Cu^{I}+15H]^{20+}$	860.8970	0.0013
21+	808.1560	$[M+21H]^{21+}$		
	811.1517	$[M+Cu^{I}+20H]^{21+}$	811.1519	-0.0002
	814.1002	$[M+2Cu^{I}+19H]^{21+}$	814.1006	-0.0004
	817.0488	$[M+3Cu^{I}+18H]^{21+}$	817.0493	-0.0005
	819.9019	$[M+2Cu^{II}+2Cu^{I}+15H]^{21+}$	819.9019	0.0000

Note: To improve the precision of each charge state, the basic molecular weight of myoglobin (M) was calculated from the corresponding observed m/z of $[M+nH]^{n+}$, and the atomic weights of H and Cu are 1.008 and 62.93, respectively, from the Orbitrap software (e.g., Thermo Xcalibur software).

Table S3. Comparison of the difference in mass-to-charge ratios between theoretical values and experimental data using a TSQ mass spectrometer after the interaction of Cu particles and myoglobin.

charge	m/z (exper.)	Cu(I)			Cu(II)		
		formula	m/z (theor.)	Δm	formula	m/z (theor.)	Δm
14+	1220.36	$[M+2Cu^{I}+12H]^{14+}$	1220.26	-0.10	$[M+2Cu^{II}+10H]^{14+}$	1220.11	-0.25
	1224.74	$[M+3Cu^{I}+11H]^{14+}$	1224.68	-0.05	$[M+3Cu^{II}+8H]^{14+}$	1224.47	-0.27
	1229.16	$[M+4Cu^{I}+10H]^{14+}$	1229.11	-0.05	$[M+4Cu^{II}+6H]^{14+}$	1228.82	-0.34
	1233.54	$[M+5Cu^{I}+9H]^{14+}$	1233.54	0.01	$[M+5Cu^{II}+4H]^{14+}$	1233.18	-0.35
	1237.96	$[M+6Cu^{I}+8H]^{14+}$	1237.97	0.01	$[M+6Cu^{II}+2H]^{14+}$	1237.54	-0.42
15+	1139.00	$[M+2Cu^{I}+13H]^{15+}$	1138.97	-0.03	$[M+2Cu^{II}+11H]^{15+}$	1138.84	-0.16
	1143.11	$[M+3Cu^{I}+12H]^{15+}$	1143.11	0.00	$[M+3Cu^{II}+9H]^{15+}$	1142.90	-0.20
	1147.24	$[M+4Cu^{I}+11H]^{15+}$	1147.24	0.00	$[M+4Cu^{II}+7H]^{15+}$	1146.97	-0.27
	1151.34	$[M+5Cu^{I}+10H]^{15+}$	1151.37	0.03	$[M+5Cu^{II}+5H]^{15+}$	1151.04	-0.30
	1155.56	$[M+6Cu^{I}+9H]^{15+}$	1155.30	-0.06	$[M+6Cu^{II}+3H]^{15+}$	1155.10	-0.46
16+	1067.86	$[M+2Cu^{I}+14H]^{16+}$	1067.85	-0.01	$[M+2Cu^{II}+12H]^{16+}$	1067.72	-0.14
	1071.71	$[M+3Cu^{I}+13H]^{16+}$	1071.73	0.02	$[M+3Cu^{II}+10H]^{16+}$	1071.54	-0.17
	1075.58	$[M+4Cu^{I}+12H]^{16+}$	1075.60	0.02	$[M+4Cu^{II}+8H]^{16+}$	1075.35	-0.23
	1079.41	$[M+5Cu^{I}+11H]^{16+}$	1079.47	0.06	$[M+5Cu^{II}+6H]^{16+}$	1079.16	-0.25
	1083.29	$[M+6Cu^{I}+10H]^{16+}$	1083.35	0.06	$[M+6Cu^{II}+4H]^{16+}$	1082.97	-0.31
17+	1004.95	$[M+2Cu^{I}+15H]^{17+}$	1005.10	0.15	$[M+2Cu^{II}+13H]^{17+}$	1004.98	0.03
	1008.70	$[M+3Cu^{I}+14H]^{17+}$	1008.74	0.05	$[M+3Cu^{II}+11H]^{17+}$	1008.56	-0.13
	1012.33	$[M+4Cu^{I}+13H]^{17+}$	1012.39	0.06	$[M+4Cu^{II}+9H]^{17+}$	1012.15	-0.18
	1015.95	$[M+5Cu^{I}+12H]^{17+}$	1016.04	0.08	$[M+5Cu^{II}+7H]^{17+}$	1015.74	-0.21
	1019.59	$[M+6Cu^{I}+11H]^{17+}$	1019.68	0.09	$[M+6Cu^{II}+5H]^{17+}$	1019.33	-0.27
18+	949.22	$[M+2Cu^{I}+16H]^{18+}$	949.31	0.09	$[M+2Cu^{II}+14H]^{18+}$	949.20	-0.02
	952.69	$[M+3Cu^{I}+15H]^{18+}$	952.76	0.07	$[M+3Cu^{II}+12H]^{18+}$	952.59	-0.10
	956.13	$[M+4Cu^{I}+14H]^{18+}$	956.20	0.07	$[M+4Cu^{II}+10H]^{18+}$	955.98	-0.15
	959.57	$[M+5Cu^{I}+13H]^{18+}$	959.64	0.08	$[M+5Cu^{II}+8H]^{18+}$	959.36	-0.20
	963.06	$[M+6Cu^{I}+12H]^{18+}$	963.09	0.02	$[M+6Cu^{II}+6H]^{18+}$	962.75	-0.31
19+	899.31	$[M+2Cu^{I}+17H]^{19+}$	899.40	0.09	$[M+2Cu^{II}+15H]^{19+}$	899.30	-0.01
	902.60	$[M+3Cu^{I}+16H]^{19+}$	902.66	0.07	$[M+3Cu^{II}+13H]^{19+}$	902.51	-0.09
	905.84	$[M+4Cu^{I}+15H]^{19+}$	905.93	0.08	$[M+4Cu^{II}+11H]^{19+}$	905.72	-0.13
	909.14	$[M+5Cu^{I}+14H]^{19+}$	909.19	0.05	$[M+5Cu^{II}+9H]^{19+}$	908.92	-0.21
	912.40	$[M+6Cu^{I}+13H]^{19+}$	912.45	0.05	$[M+6Cu^{II}+7H]^{19+}$	912.13	-0.27
20+	854.31	$[M+2Cu^{I}+18H]^{20+}$	854.48	0.17	$[M+2Cu^{II}+16H]^{20+}$	854.38	0.07
	857.49	$[M+3Cu^{I}+17H]^{20+}$	857.58	0.09	$[M+3Cu^{II}+14H]^{20+}$	857.43	-0.06
	860.60	$[M+4Cu^{I}+16H]^{20+}$	860.68	0.08	$[M+4Cu^{II}+12H]^{20+}$	860.48	-0.12
	863.73	$[M+5Cu^{I}+15H]^{20+}$	863.78	0.05	$[M+5Cu^{II}+10H]^{20+}$	863.53	-0.20
	866.74	$[M+6Cu^{I}+14H]^{20+}$	866.88	0.14	$[M+6Cu^{II}+8H]^{20+}$	866.58	-0.16
21+	813.66	$[M+2Cu^{I}+19H]^{21+}$	813.84	0.18	$[M+2Cu^{II}+17H]^{21+}$	813.74	0.09
	816.70	$[M+3Cu^{I}+18H]^{21+}$	816.79	0.09	$[M+3Cu^{II}+15H]^{21+}$	816.65	-0.05
	819.64	$[M+4Cu^{I}+17H]^{21+}$	819.74	0.11	$[M+4Cu^{II}+13H]^{21+}$	819.55	-0.08
	822.72	$[M+5Cu^{I}+16H]^{21+}$	822.70	-0.03	$[M+5Cu^{II}+11H]^{21+}$	822.46	-0.27
	825.59	$[M+6Cu^{I}+15H]^{21+}$	825.65	0.06	$[M+6Cu^{II}+9H]^{21+}$	825.36	-0.23

Table S4. Comparison of the difference in mass-to-charge ratios between theoretical values and experimental data using an Orbitrap mass spectrometer after the interaction of Cu nanoparticles and myoglobin.

charge	m/z (exper.)	formula	m/z (theor.)	Δm
17+	1012.7573	$[M+4Cu^{I}+13H]^{17+}$	1012.7015	0.0558
		$[M+Cu^{II}+3Cu^{I}+12H]^{17+}$	1012.6422	0.1151
		$[M+2Cu^{II}+2Cu^{I}+11H]^{17+}$	1012.5829	0.1744
		$[M+3Cu^{II}+Cu^{I}+10H]^{17+}$	1012.5236	0.2337
		$[M+4Cu^{II}+9H]^{17+}$	1012.4643	0.2930
17+	1016.5766	$[M+5Cu^{I}+12H]^{17+}$	1016.3440	0.2326
		$[M+Cu^{II}+4Cu^{I}+11H]^{17+}$	1016.2847	0.2919
		$[M+2Cu^{II}+3Cu^{I}+10H]^{17+}$	1016.2254	0.3512
		$[M+3Cu^{II}+2Cu^{I}+9H]^{17+}$	1016.1661	0.4105
		$[M+4Cu^{II}+Cu^{I}+8H]^{17+}$	1016.1068	0.4698
		$[M+5Cu^{II}+7H]^{17+}$	1016.0475	0.5291
17+	1020.2192	$[M+6Cu^{I}+11H]^{17+}$	1019.9865	0.2327
		$[M+Cu^{II}+5Cu^{I}+10H]^{17+}$	1019.9272	0.2920
		$[M+2Cu^{II}+4Cu^{I}+9H]^{17+}$	1019.8679	0.3513
		$[M+3Cu^{II}+3Cu^{I}+8H]^{17+}$	1019.8086	0.4106
		$[M+4Cu^{II}+2Cu^{I}+7H]^{17+}$	1019.7493	0.4699
		$[M+5Cu^{II}+Cu^{I}+6H]^{17+}$	1019.6900	0.5292
		$[M+6Cu^{II}+5H]^{17+}$	1019.6307	0.5885
17+	1023.8020	$[M+7Cu^{I}+10H]^{17+}$	1023.6289	0.1731
		$[M+Cu^{II}+6Cu^{I}+9H]^{17+}$	1023.5696	0.2324
		$[M+2Cu^{II}+5Cu^{I}+8H]^{17+}$	1023.5103	0.2917
		$[M+3Cu^{II}+4Cu^{I}+7H]^{17+}$	1023.4510	0.3510
		$[M+4Cu^{II}+3Cu^{I}+6H]^{17+}$	1023.3918	0.4102
		$[M+5Cu^{II}+2Cu^{I}+5H]^{17+}$	1023.3325	0.4695
		$[M+6Cu^{II}+Cu^{I}+4H]^{17+}$	1023.2732	0.5288
		$[M+7Cu^{II}+3H]^{17+}$	1023.2139	0.5881
17+	1027.5046	$[M+8Cu^{I}+9H]^{17+}$	1027.2714	0.2332
		$[M+Cu^{II}+7Cu^{I}+8H]^{17+}$	1027.2121	0.2925
		$[M+2Cu^{II}+6Cu^{I}+7H]^{17+}$	1027.1528	0.3518
		$[M+3Cu^{II}+5Cu^{I}+6H]^{17+}$	1027.0935	0.4111
		$[M+4Cu^{II}+4Cu^{I}+5H]^{17+}$	1027.0342	0.4704
		$[M+5Cu^{II}+3Cu^{I}+4H]^{17+}$	1026.9749	0.5297
		$[M+6Cu^{II}+2Cu^{I}+3H]^{17+}$	1026.9156	0.5890
		$[M+7Cu^{II}+Cu^{I}+2H]^{17+}$	1026.8563	0.6483
		$[M+8Cu^{II}+H]^{17+}$	1026.7970	0.7076
17+	1031.1464	$[M+9Cu^{I}+8H]^{17+}$	1030.9139	0.2325
		$[M+Cu^{II}+8Cu^{I}+7H]^{17+}$	1030.8546	0.2918
		$[M+2Cu^{II}+7Cu^{I}+6H]^{17+}$	1030.7953	0.3511
		$[M+3Cu^{II}+6Cu^{I}+5H]^{17+}$	1030.7360	0.4104
		$[M+4Cu^{II}+5Cu^{I}+4H]^{17+}$	1030.6767	0.4697
		$[M+5Cu^{II}+4Cu^{I}+3H]^{17+}$	1030.6174	0.5290
		$[M+6Cu^{II}+3Cu^{I}+2H]^{17+}$	1030.5581	0.5883
		$[M+7Cu^{II}+2Cu^{I}+H]^{17+}$	1030.4988	0.6476

Continued to the above

		[M+8Cu^{II}+Cu^{I}]$^{17+}$	1030.4395	0.7069
16+	1075.9919	[M+4Cu^{I}+12H]$^{16+}$	1075.9324	0.0595
		[M+Cu^{II}+3Cu^{I}+11H]$^{16+}$	1075.8694	0.1225
		[M+2Cu^{II}+2Cu^{I}+10H]$^{16+}$	1075.8064	0.1855
		[M+3Cu^{II}+Cu^{I}+9H]$^{16+}$	1075.7434	0.2485
		[M+4Cu^{II}+8H]$^{16+}$	1075.6804	0.3115
16+	1079.9252	[M+5Cu^{I}+11H]$^{16+}$	1079.8025	0.1227
		[M+Cu^{II}+4Cu^{I}+10H]$^{16+}$	1079.7395	0.1857
		[M+2Cu^{II}+3Cu^{I}+9H]$^{16+}$	1079.6765	0.2487
		[M+3Cu^{II}+2Cu^{I}+8H]$^{16+}$	1079.6135	0.3117
		[M+4Cu^{II}+Cu^{I}+7H]$^{16+}$	1079.5505	0.3747
		[M+5Cu^{II}+6H]$^{16+}$	1079.4875	0.4377
16+	1083.9205	[M+6Cu^{I}+10H]$^{16+}$	1083.6726	0.2479
		[M+Cu^{II}+5Cu^{I}+9H]$^{16+}$	1083.6096	0.3109
		[M+2Cu^{II}+4Cu^{I}+8H]$^{16+}$	1083.5466	0.3739
		[M+3Cu^{II}+3Cu^{I}+7H]$^{16+}$	1083.4836	0.4369
		[M+4Cu^{II}+2Cu^{I}+6H]$^{16+}$	1083.4206	0.4999
		[M+5Cu^{II}+Cu^{I}+5H]$^{16+}$	1083.3576	0.5629
		[M+6Cu^{II}+4H]$^{16+}$	1083.2946	0.6259
16+	1087.7886	[M+7Cu^{I}+9H]$^{16+}$	1087.5427	0.2459
		[M+Cu^{II}+6Cu^{I}+8H]$^{16+}$	1087.4797	0.3089
		[M+2Cu^{II}+5Cu^{I}+7H]$^{16+}$	1087.4167	0.3719
		[M+3Cu^{II}+4Cu^{I}+6H]$^{16+}$	1087.3537	0.4349
		[M+4Cu^{II}+3Cu^{I}+5H]$^{16+}$	1087.2907	0.4979
		[M+5Cu^{II}+2Cu^{I}+4H]$^{16+}$	1087.2277	0.5609
		[M+6Cu^{II}+Cu^{I}+3H]$^{16+}$	1087.1647	0.6239
		[M+7Cu^{II}+2H]$^{16+}$	1087.1017	0.6869
16+	1091.5954	[M+8Cu^{I}+8H]$^{16+}$	1091.4129	0.1825
		[M+Cu^{II}+7Cu^{I}+7H]$^{16+}$	1091.3499	0.2455
		[M+2Cu^{II}+6Cu^{I}+6H]$^{16+}$	1091.2869	0.3085
		[M+3Cu^{II}+5Cu^{I}+5H]$^{16+}$	1091.2239	0.3715
		[M+4Cu^{II}+4Cu^{I}+4H]$^{16+}$	1091.1609	0.4345
		[M+5Cu^{II}+3Cu^{I}+3H]$^{16+}$	1091.0979	0.4975
		[M+6Cu^{II}+2Cu^{I}+2H]$^{16+}$	1091.0349	0.5605
		[M+7Cu^{II}+Cu^{I}+H]$^{16+}$	1090.9719	0.6235
		[M+8Cu^{II}]$^{16+}$	1090.9089	0.6865
16+	1095.7182	[M+9Cu^{I}+7H]$^{16+}$	1095.2830	0.4352
		[M+Cu^{II}+8Cu^{I}+6H]$^{16+}$	1095.2200	0.4982
		[M+2Cu^{II}+7Cu^{I}+5H]$^{16+}$	1095.1570	0.5612
		[M+3Cu^{II}+6Cu^{I}+4H]$^{16+}$	1095.0940	0.6242
		[M+4Cu^{II}+5Cu^{I}+3H]$^{16+}$	1095.0310	0.6872
		[M+5Cu^{II}+4Cu^{I}+2H]$^{16+}$	1094.9680	0.7502
		[M+6Cu^{II}+3Cu^{I}+H]$^{16+}$	1094.9050	0.8132
		[M+7Cu^{II}+2Cu^{I}]$^{16+}$	1094.8420	0.9762

Note: To improve the precision of each charge state, the basic molecular weight of myoglobin (M) was calculated from the corresponding observed m/z of $[M+nH]^{n+}$, and the atomic weights of H and Cu are 1.008 and 62.93, respectively, from the Orbitrap software (e.g., Thermo Xcalibur software).

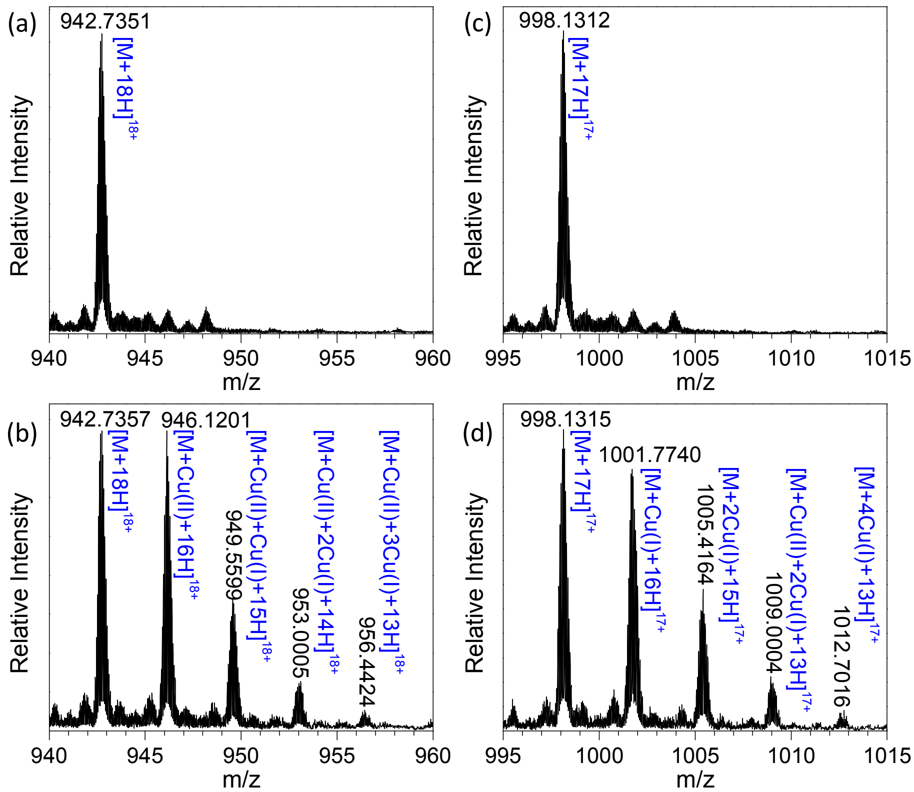

Figure S1. Comparison of the mass spectra of [**(a)** and **(c)**] myoglobin and [**(b)** and **(d)**] myoglobin/$Cu(NO_3)_2$ with a high resolution Orbitrap mass spectrometer: **(a)** myoglobin with a charge state of 18+, **(b)** myoglobin and $Cu(NO_3)_2$ with a charge state of 18+, **(c)** myoglobin with a charge state of 17+, **(d)** myoglobin and $Cu(NO_3)_2$ with a charge state of 17+ with nanoESI (Note: concentration of $Cu(NO_3)_2$ solution: 500 μg mL^{-1} with methanol as solvent, sample: 100 μg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).

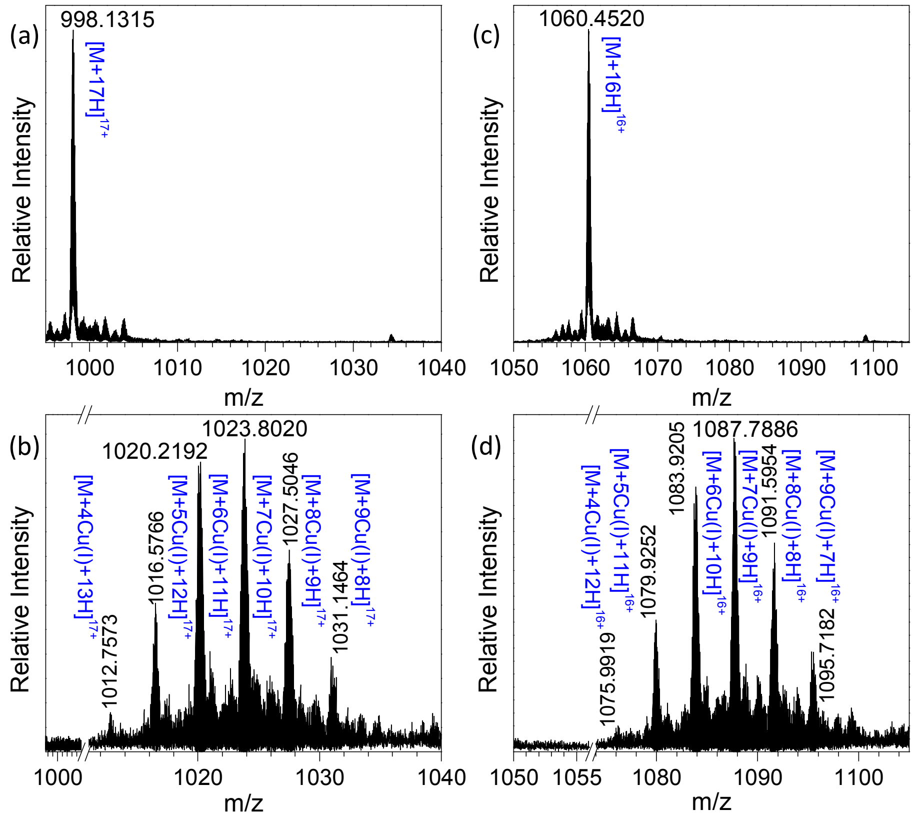

Figure S2. Comparison of the mass spectra of [**(a)** and **(c)**] myoglobin and [**(b)** and **(d)**] myoglobin/Cu nanoparticles with a high resolution Orbitrap mass spectrometer: **(a)** myoglobin with a charge state of 17+, **(b)** myoglobin and Cu nanoparticles with a charge state of 17+, **(c)** myoglobin with a charge state of 16+, **(d)** myoglobin and Cu nanoparticles with a charge state of 16+ with nanoESI (Note: concentration of Cu nanoparticle solution: 500 µg mL^{-1} with methanol as solvent, sample: 100 µg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).

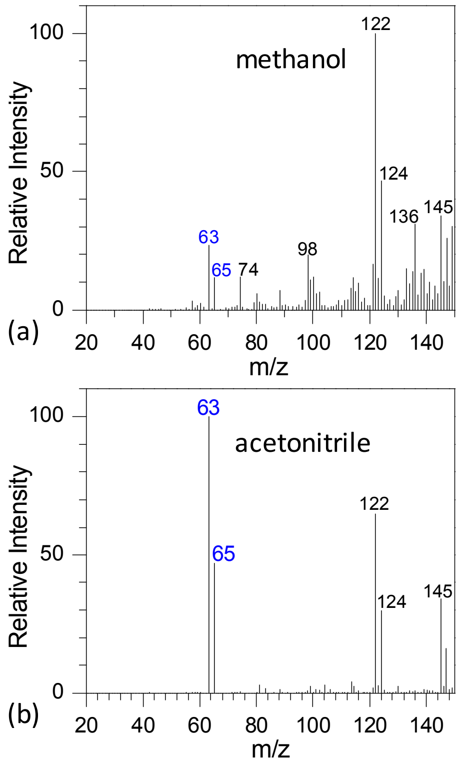

Figure S3. Mass spectrum of Cu particles using **(a)** methanol and **(b)** acetonitrile as solvent with nanoESI (concentration of Cu nanoparticle solution: 500 µg mL^{-1}, spray voltage: 1.4 kV).

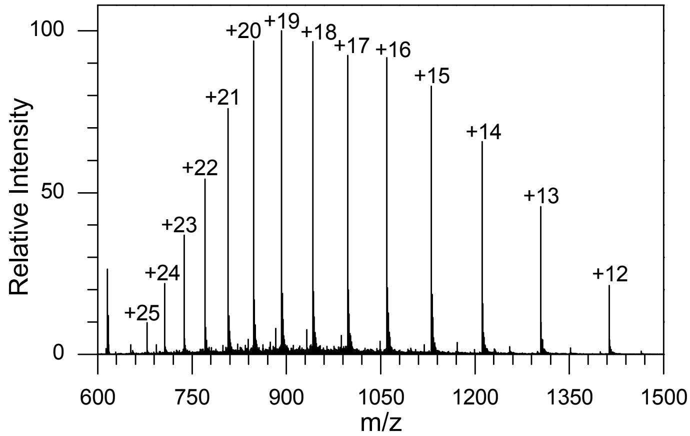

Figure S4**.** Mass spectra by first loading 10 µL myoglobin solution followed by 10 µL Cu nanoparticle solution (solvent for dissolving Cu nanoparticles: methanol, sample: 100 µg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, spray voltage: 1.4 kV).

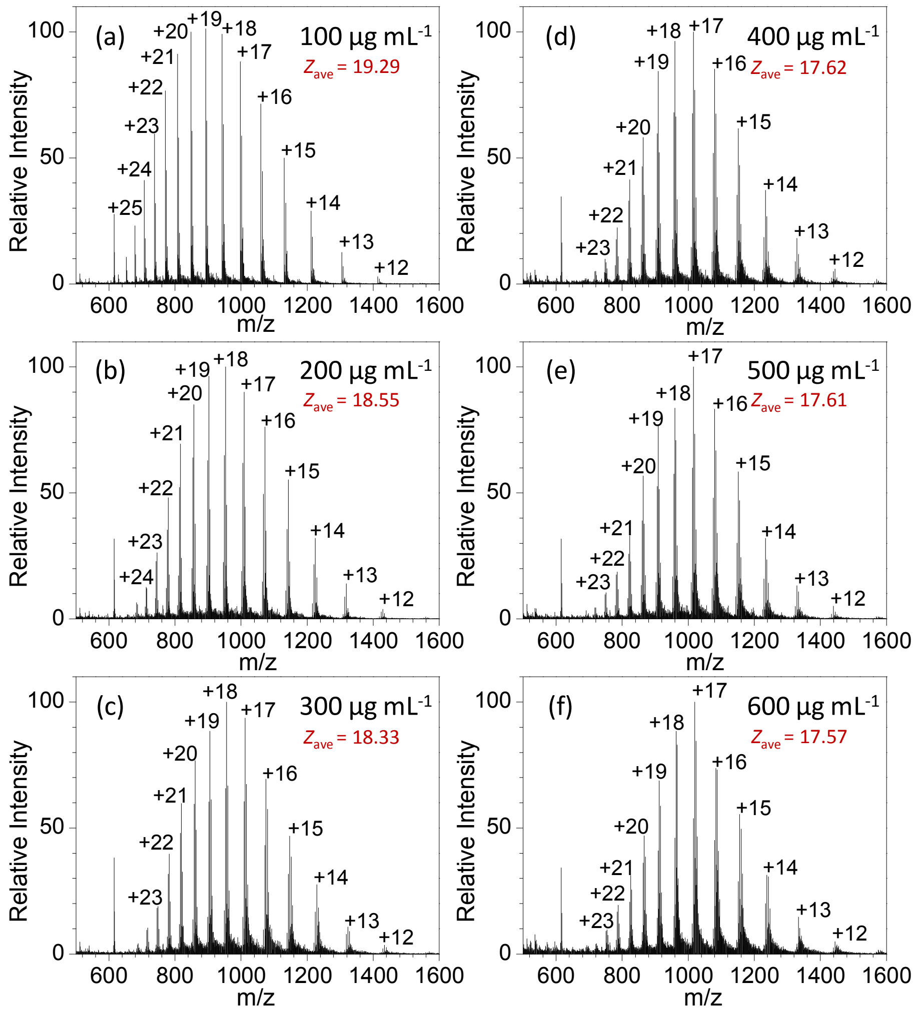

Figure S5**.** Effect of the concentration of Cu nanoparticles on the interaction between Cu^{+} and myoglobin in the process of matrix-assisted nanoESI: **(a)** 100 µg mL^{-1}, **(b)** 200 µg mL^{-1}, **(c)** 300 µg mL^{-1}, **(d)** 400 µg mL^{-1}, **(e)** 500 µg mL^{-1}, and **(f)** 600 µg mL^{-1} (solvent for dissolving Cu nanoparticles: methanol, sample: 100 µg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, spray voltage: 1.4 kV).

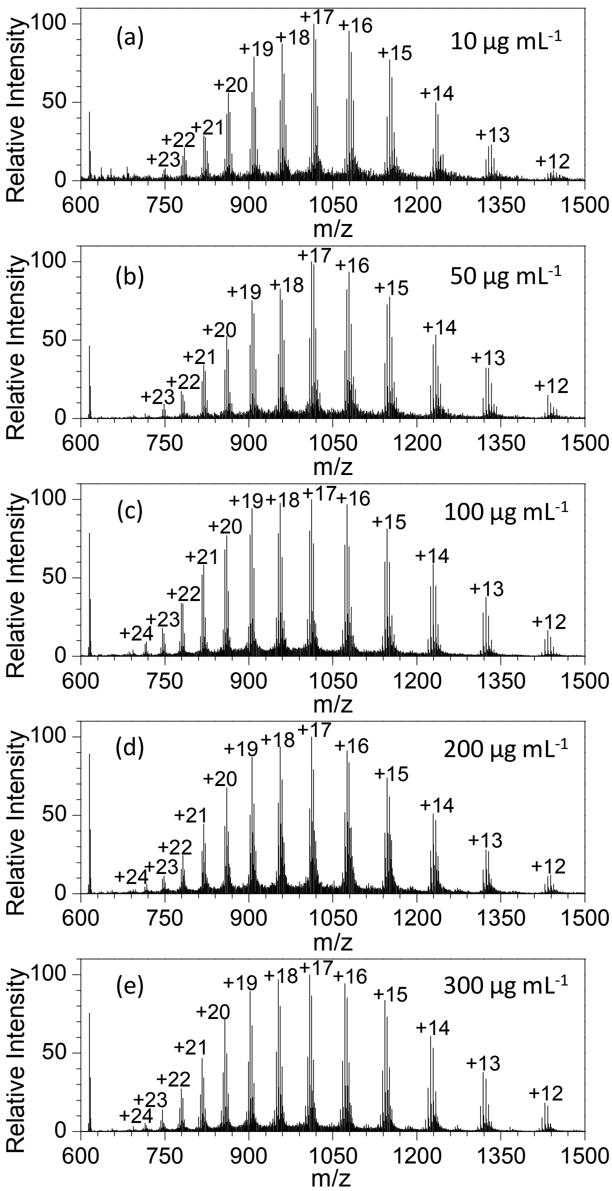

***Figure S6*.** Effect of the concentration of **(a)**-**(e)** myoglobin solution ranging from 10 to 300 µg mL^{-1} as indicated on the interactions between Cu and myoglobin (Note: sample: myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).

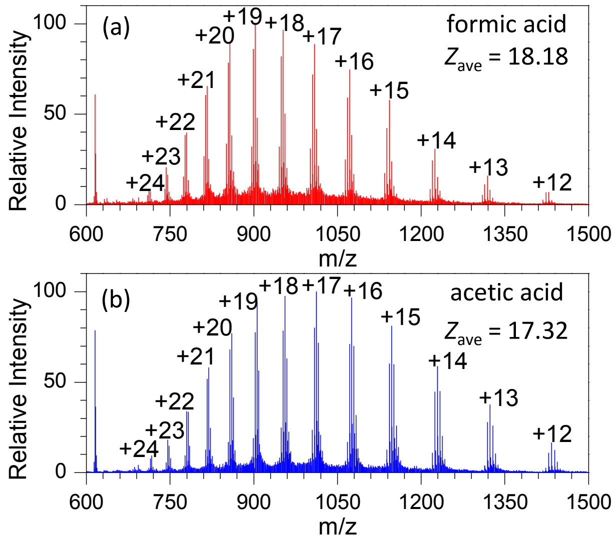

Figure S7. Comparison of the performance of developed MANESI in analysis of myoglobin samples by adding **(a)** 0.5% formic acid and **(b)** 0.5% acetic acid (Note: concentration of Cu solution: 500 µg mL^{-1} with methanol as solvent, sample: 100 µg mL^{-1} myoglobin, applied voltage: 1.4 kV).

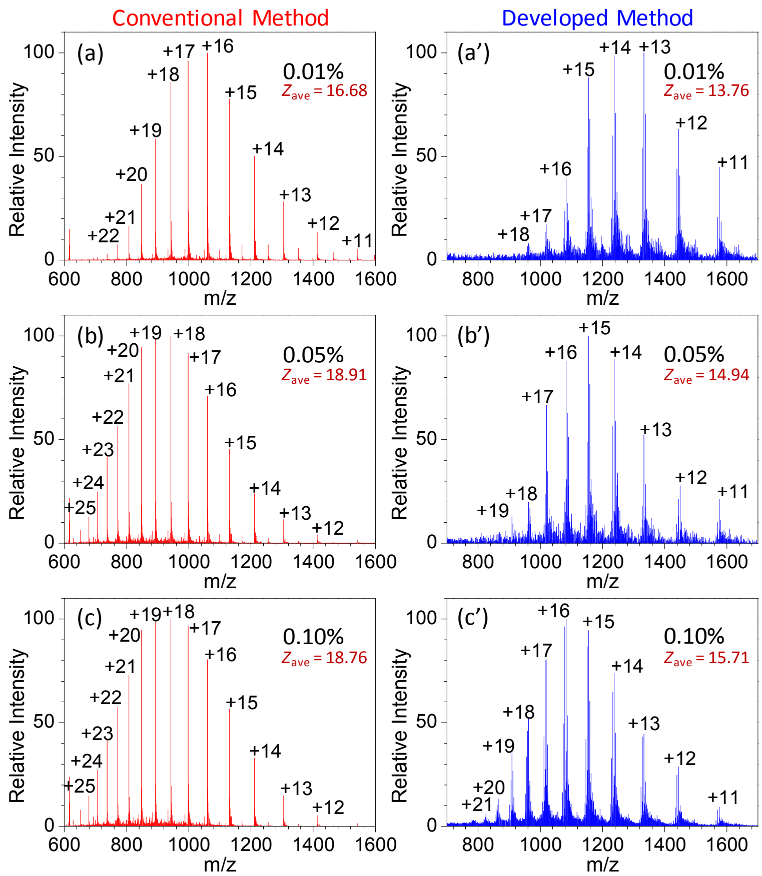

Figure S8. Comparison of the performance of **(a)**-**(c)** conventional nanoESI and **(a')**-**(c')** developed MANESI in analysis of myoglobin samples containing different percentages of acetic acid (Note: concentration of Cu solution: 500 µg mL^{-1} with methanol as solvent, sample: 100 µg mL^{-1} myoglobin, applied voltage: 1.4 kV).

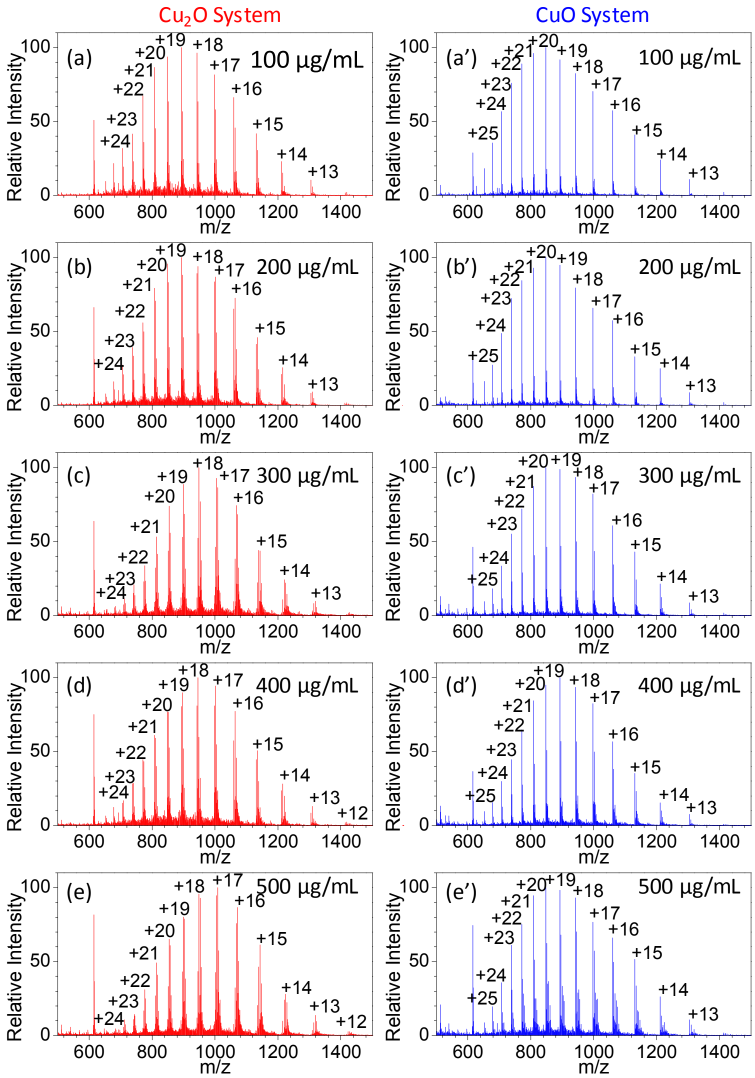

Figure S9. Effect of the concentrations of **(a)-(e)** Cu_2O and **(a')-(e')** CuO ranging from 100 to 500 μg/mL as indicated on the interactions between Cu and myoglobin (Note: sample: 100 μg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).

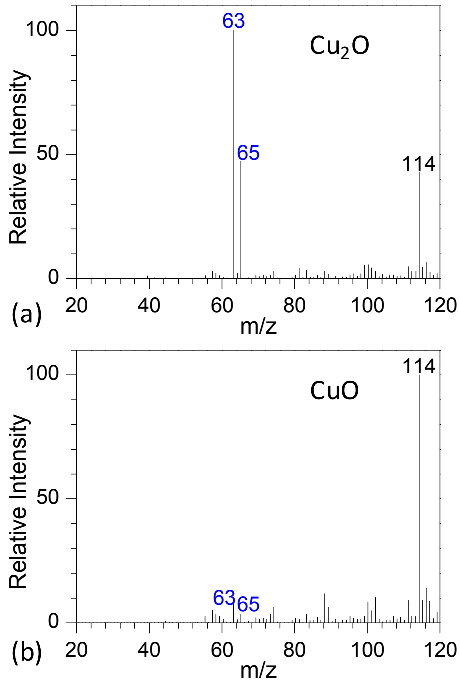

Figure S10. Mass spectrum of **(a)** Cu_2O particles and **(b)** CuO particles using acetonitrile as solvent with nanoESI (concentration of Cu_2O or CuO nanoparticle solution: 500 µg mL^{-1}, spray voltage: 1.4 kV).

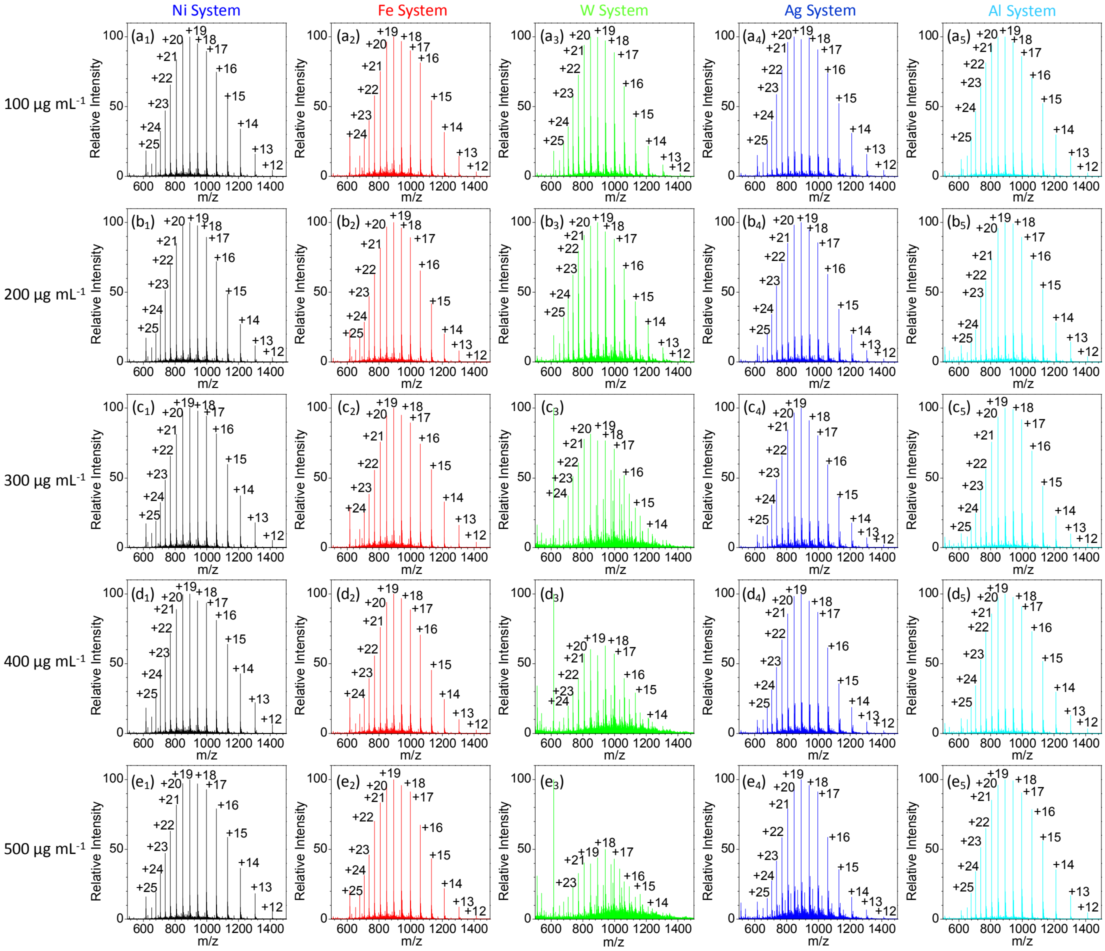

Figure S11. Effect of the concentrations of [**(a₁)-(e₁)**] Ni, [**(a₂)-(e₂)**] Fe, [**(a₃)-(e₃)**] W, [**(a₄)-(e₄)**] Ag, and [**(a₅)-(e₅)**] Al nanoparticles ranging from 100 to 500 μg/mL as indicated on the interactions between Cu and myoglobin (Note: sample: 100 μg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).

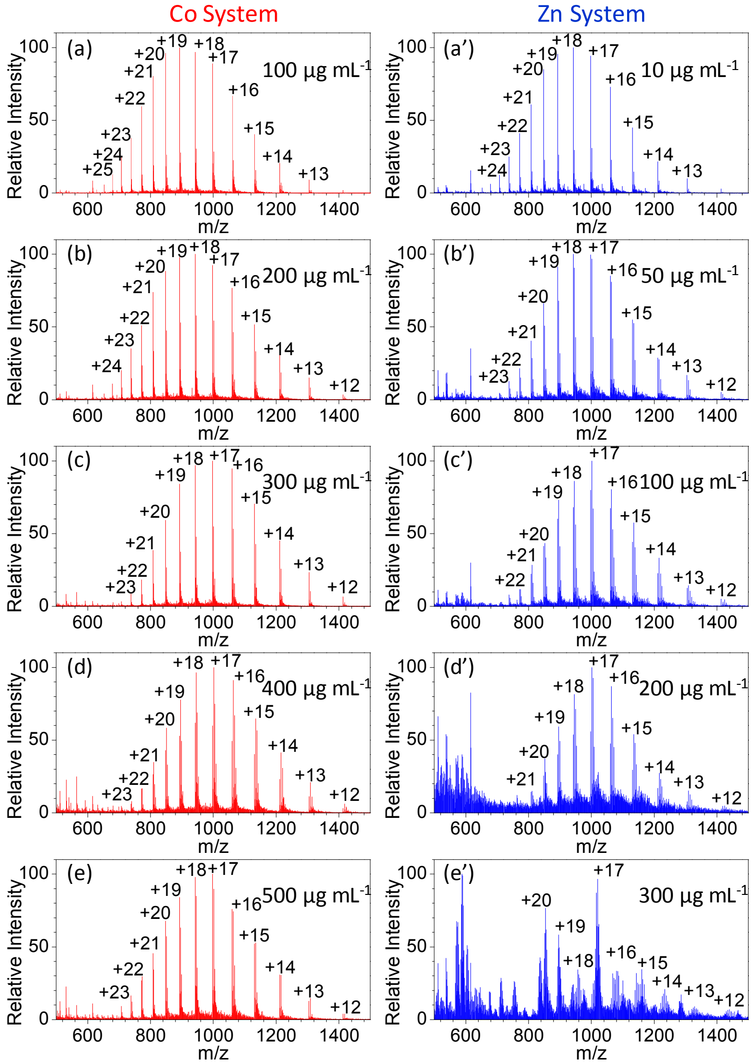

***Figure S12*.** Effect of the concentrations of [**(a)**-**(e)**] Co and [**(a')**-**(e')**] Zn nanoparticles ranging from 100 to 500 µg/mL as indicated on the interactions between Cu and myoglobin (Note: sample: 100 µg mL^{-1} myoglobin in 1:1 methanol/water containing 0.5% acetic acid, applied voltage: 1.4 kV).