

Supplementary Information

Table S1. Mulliken charge distribution in methionine-containing dipeptides and the corresponding cation radicals.

Compound	Mulliken Charge Value			
	S14	C9	C5	C3
Gly-Met z = 0	0.028	-0.609	0.198	-0.421
Gly-Met cation radical z = +1	0.480	-0.479	-0.145	-0.540
Ala-Met z = 0	0.085	-0.836	0.137	-0.299
Ala-Met cation radical z = +1	0.487	-0.480	-0.174	-0.515
Val-Met z = 0	0.091	-0.839	0.144	-0.307
Val-Met cation radical z = +1	0.481	-0.502	-0.125	-0.573
Leu-Met z = 0	0.097	-0.876	0.150	-0.297
Leu-Met cation radical z = +1	0.477	-0.483	-0.152	-0.552
Ile-Met z = 0	0.098	-0.853	0.145	-0.284
Ile-Met cation radical z = +1	0.483	-0.506	-0.117	-0.576
Phe-Met z = 0	0.092	-0.871	0.158	-0.298
Phe-Met cation radical z = +1	0.473	-0.488	-0.143	-0.549
Pro-Met z = 0	0.072	-0.835	0.149	-0.524
Pro-Met cation radical z = +1	0.455	-0.498	-0.137	-0.486
Met-Met z = 0 C/N	0.047/0.085	-0.990/-0.471	0.344/-0.443	-0.320/0.528
Met-Met cation radical z = +1 C/N	0.275/0.108	-0.669/-0.480	0.202/-0.508	-0.631/0.128
Cys-Met z = 0 Met/Cys	0.032/-0.008	-0.648/-0.511	0.325/-	-0.623/-0.235
Cys-Met cation radical z = +1 Met/Cys	0.489/0.095	-0.491/-0.430	-0.131/-	-0.532/-0.287
Asn-Met z = 0	0.094	-0.832	0.107	-0.277
Asn-Met cation radical z = +1	0.466	-0.482	-0.169	-0.586
Asp-Met z = -1	-0.002	-0.718	0.066	-0.805
Asp-Met cation radical z = 0	0.373	-0.519	-0.105	-0.426
Gln-Met z = 0	0.013	-0.741	0.272	-0.541
Gln-Met cation radical z = +1	0.481	-0.510	-0.079	-0.486
Glu-Met z = -1	0	-0.698	0.045	-0.750
Glu-Met cation radical z = 0	0.375	-0.524	-0.071	-0.442
Lys-Met z = 1	0.049	-0.625	0.092	-0.169
Lys-Met cation radical z = +2	0.529	-0.488	-0.167	-0.541
Arg-Met z = 1	0.097	-0.695	0.360	-0.850
Arg-Met cation radical z = +2	0.530	-0.488	-0.167	-0.540
Ser-Met z = 0	0.012	-0.652	0.158	-0.730
Ser-Met cation radical z = +1	0.440	-0.512	-0.120	-0.544
Thr-Met z = 0	0.095	-0.879	0.147	-0.254
Thr-Met cation radical z = +1	0.444	-0.509	-0.141	-0.508
His-Met z = 0	0.110	-0.440	-0.207	-0.334
His-Met cation radical z = +1	0.260	-0.459	-0.219	-0.304
Trp-Met z = 0	0.07	-0.410	-0.018	-0.495
Trp-Met cation radical z = +1	0.108	-0.507	0.002	-0.304
Met-Gly z = 0	-0.008	-0.459	-0.349	0.343
Met-Gly cation radical z = +1	0.117	-0.586	-0.317	0.012
Met-Ala z = 0	-0.017	-0.435	-0.361	-0.030

Table S1. *Cont.*

Compound	Mulliken Charge Value			
	S14	C9	C5	C3
Met-Ala cation radical $z = +1$	0.131	-0.531	-0.404	0.172
Met-Val $z = 0$	0.090	-0.642	-0.171	0.231
Met-Val cation radical $z = +1$	0.108	-0.556	-0.428	0.353
Met-Leu $z = 0$	0.072	-0.427	-0.446	0.440
Met-Leu cation radical $z = +1$	0.104	-0.519	-0.434	0.262
Met-Ile $z = 0$	0.083	-0.663	-0.151	0.279
Met-Ile cation radical $z = +1$	0.105	-0.566	-0.415	0.306
Met-Phe $z = 0$	0.044	-0.518	-0.223	-0.259
Met-Phe cation radical $z = +1$	0.114	-0.622	-0.175	-0.275
Met-Pro $z = 0$	0.061	-0.468	-0.269	0.156
Met-Pro cation radical $z = +1$	0.179	-0.536	-0.163	-0.188
Met-Cys $z = 0$ Met/Cys	0.086/0.021	-0.480/-0.450	-0.396/-	0.398/-0.152
Met-Cys cation radical $z = +1$ Met/Cys	0.116/0.326	-0.481/-0.350	-0.451/-	0.135/-0.237
Met-Asn $z = 0$	0.086	-0.464	-0.419	0.463
Met-Asn cation radical $z = +1$	0.114	-0.468	-0.533	0.200
Met-Asp $z = -1$	0.022	-0.319	-0.378	0.347
Met-Asp cation radical $z = 0$	0.089	-0.470	-0.432	0.453
Met-Gln $z = 0$	0.018	-0.589	-0.176	-0.369
Met-Gln cation radical $z = +1$	0.112	-0.621	-0.185	-0.350
Met-Glu $z = -1$	0.050	-0.666	-0.102	-0.277
Met-Glu cation radical $z = 0$	0.009	-0.591	-0.140	-0.431
Met-Lys $z = 1$	0.069	-0.624	-0.191	-0.281
Met-Lys cation radical $z = +2$	0.438	-0.436	-0.397	-0.093
Met-Arg $z = 1$	0.057	-0.622	-0.169	-0.229
Met-Arg cation radical $z = +2$	0.336	-0.455	-0.302	-0.164
Met-Ser $z = 0$	0.090	-0.464	-0.415	0.538
Met-Ser cation radical $z = +1$	0.116	-0.477	-0.461	0.160
Met-Thr $z = 0$	0.026	-0.585	-0.160	-0.347
Met-Thr cation radical $z = +1$	0.097	-0.647	-0.161	-0.316
Met-His $z = 0$	0	-0.452	-0.382	0.387
Met-His cation radical $z = +1$	-0.04	-0.517	-0.369	0.098
Met-Trp $z = 0$	0.033	-0.493	-0.534	0.387
Met-Trp cation radical $z = +1$	0.140	-0.567	-0.483	0.527

Table S2. The electron density distribution and the bond length of O–H in aromatic systems of tyrosine-containing dipeptides and related radicals and the corresponding cation-radicals.

Compound	Mulliken Charge Value			
	S14	C9	C5	C3
Gly-Met $z = 0$	0.028	−0.609	0.198	−0.421
Gly-Met cation radical $z = +1$	0.480	−0.479	−0.145	−0.540
Ala-Met $z = 0$	0.085	−0.836	0.137	−0.299
Ala-Met cation radical $z = +1$	0.487	−0.480	−0.174	−0.515
Val-Met $z = 0$	0.091	−0.839	0.144	−0.307
Val-Met cation radical $z = +1$	0.481	−0.502	−0.125	−0.573
Leu-Met $z = 0$	0.097	−0.876	0.150	−0.297
Leu-Met cation radical $z = +1$	0.477	−0.483	−0.152	−0.552
Ile-Met $z = 0$	0.098	−0.853	0.145	−0.284
Ile-Met cation radical $z = +1$	0.483	−0.506	−0.117	−0.576
Phe-Met $z = 0$	0.092	−0.871	0.158	−0.298
Phe-Met cation radical $z = +1$	0.473	−0.488	−0.143	−0.549
Pro-Met $z = 0$	0.072	−0.835	0.149	−0.524
Pro-Met cation radical $z = +1$	0.455	−0.498	−0.137	−0.486
Met-Met $z = 0$ C/N	0.047/0.085	−0.990/−0.471	0.344/−0.443	−0.320/0.528
Met-Met cation radical $z = +1$ C/N	0.275/0.108	−0.669/−0.480	0.202/−0.508	−0.631/0.128
Cys-Met $z = 0$ Met/Cys	0.032/−0.008	−0.648/−0.511	0.325/−	−0.623/−0.235
Cys-Met cation radical $z = +1$ Met/Cys	0.489/0.095	−0.491/−0.430	−0.131/−	−0.532/−0.287
Asn-Met $z = 0$	0.094	−0.832	0.107	−0.277
Asn-Met cation radical $z = +1$	0.466	−0.482	−0.169	−0.586
Asp-Met $z = -1$	−0.002	−0.718	0.066	−0.805
Asp-Met cation radical $z = 0$	0.373	−0.519	−0.105	−0.426
Gln-Met $z = 0$	0.013	−0.741	0.272	−0.541
Gln-Met cation radical $z = +1$	0.481	−0.510	−0.079	−0.486
Glu-Met $z = -1$	0	−0.698	0.045	−0.750
Glu-Met cation radical $z = 0$	0.375	−0.524	−0.071	−0.442
Lys-Met $z = 1$	0.049	−0.625	0.092	−0.169
Lys-Met cation radical $z = +2$	0.529	−0.488	−0.167	−0.541
Arg-Met $z = 1$	0.097	−0.695	0.360	−0.850
Arg-Met cation radical $z = +2$	0.530	−0.488	−0.167	−0.540
Ser-Met $z = 0$	0.012	−0.652	0.158	−0.730
Ser-Met cation radical $z = +1$	0.440	−0.512	−0.120	−0.544
Thr-Met $z = 0$	0.095	−0.879	0.147	−0.254
Thr-Met cation radical $z = +1$	0.444	−0.509	−0.141	−0.508
His-Met $z = 0$	0.110	−0.440	−0.207	−0.334
His-Met cation radical $z = +1$	0.260	−0.459	−0.219	−0.304
Trp-Met $z = 0$	0.07	−0.410	−0.018	−0.495
Trp-Met cation radical $z = +1$	0.108	−0.507	0.002	−0.304
Met-Gly $z = 0$	−0.008	−0.459	−0.349	0.343

Table S2. *Cont.*

Compound	Mulliken Charge Value			
	S14	C9	C5	C3
Met-Gly cation radical $z = +1$	0.117	-0.586	-0.317	0.012
Met-Ala $z = 0$	-0.017	-0.435	-0.361	-0.030
Met-Ala cation radical $z = +1$	0.131	-0.531	-0.404	0.172
Met-Val $z = 0$	0.090	-0.642	-0.171	0.231
Met-Val cation radical $z = +1$	0.108	-0.556	-0.428	0.353
Met-Leu $z = 0$	0.072	-0.427	-0.446	0.440
Met-Leu cation radical $z = +1$	0.104	-0.519	-0.434	0.262
Met-Ile $z = 0$	0.083	-0.663	-0.151	0.279
Met-Ile cation radical $z = +1$	0.105	-0.566	-0.415	0.306
Met-Phe $z = 0$	0.044	-0.518	-0.223	-0.259
Met-Phe cation radical $z = +1$	0.114	-0.622	-0.175	-0.275
Met-Pro $z = 0$	0.061	-0.468	-0.269	0.156
Met-Pro cation radical $z = +1$	0.179	-0.536	-0.163	-0.188
Met-Cys $z = 0$ Met/Cys	0.086/0.021	-0.480/-0.450	-0.396/-	0.398/-0.152
Met-Cys cation radical $z = +1$ Met/Cys	0.116/0.326	-0.481/-0.350	-0.451/-	0.135/-0.237
Met-Asn $z = 0$	0.086	-0.464	-0.419	0.463
Met-Asn cation radical $z = +1$	0.114	-0.468	-0.533	0.200
Met-Asp $z = -1$	0.022	-0.319	-0.378	0.347
Met-Asp cation radical $z = 0$	0.089	-0.470	-0.432	0.453
Met-Gln $z = 0$	0.018	-0.589	-0.176	-0.369
Met-Gln cation radical $z = +1$	0.112	-0.621	-0.185	-0.350
Met-Glu $z = -1$	0.050	-0.666	-0.102	-0.277
Met-Glu cation radical $z = 0$	0.009	-0.591	-0.140	-0.431
Met-Lys $z = 1$	0.069	-0.624	-0.191	-0.281
Met-Lys cation radical $z = +2$	0.438	-0.436	-0.397	-0.093
Met-Arg $z = 1$	0.057	-0.622	-0.169	-0.229
Met-Arg cation radical $z = +2$	0.336	-0.455	-0.302	-0.164
Met-Ser $z = 0$	0.090	-0.464	-0.415	0.538
Met-Ser cation radical $z = +1$	0.116	-0.477	-0.461	0.160
Met-Thr $z = 0$	0.026	-0.585	-0.160	-0.347
Met-Thr cation radical $z = +1$	0.097	-0.647	-0.161	-0.316
Met-His $z = 0$	0	-0.452	-0.382	0.387
Met-His cation radical $z = +1$	-0.04	-0.517	-0.369	0.098
Met-Trp $z = 0$	0.033	-0.493	-0.534	0.387
Met-Trp cation radical $z = +1$	0.140	-0.567	-0.483	0.527

Table S3. Thermodynamic and energy parameters of the methionine-containing dipeptides in the gas phase (298 K).

Compound	EBD, kCal/mol	IPe, eV	IPO, eV	E _{HOMO} , eV	E _{LUMO} , eV	χ , eV
Gly-Met (z = 0)	-	7.46	5.89	-5.89	-1.17	3.52
Ala-Met (z = 0)	-	7.49	6.08	-6.08	-0.97	3.53
Val-Met (z = 0)	-	7.43	6.08	-6.08	-0.89	3.48
Leu-Met (z = 0)	-	7.40	6.06	-6.06	-0.89	3.48
Ile-Met (z = 0)	-	7.40	6.07	-6.07	-0.87	3.47
Phe-Met (z = 0)	-	7.40	6.09	-6.09	-0.89	3.49
Pro-Met (z = 0)	-	6.31	5.29	-5.29	-1.73	3.51
Met-Met (z = 0)	-	7.49	5.92	-5.92	-1.15	3.53
Cys-Met (z = 0)	88.47 (Cys)	7.80	5.88	-5.88	-1.29	3.58
Asn-Met (z = 0)	-	7.26	6.09	-6.09	-0.84	3.46
Asp-Met (z = -1)	-	4.02	2.80	-2.80	2.06	0.37
Gln-Met (z = 0)	-	6.73	5.97	-5.97	-1.92	3.94
Glu-Met (z = -1)	-	3.99	2.77	-2.77	1.88	0.44
Lys-Met (z = 1)	-	10.42	8.57	-8.57	-4.18	6.38
Arg-Met (z = 1)	-	9.46	7.85	-7.85	-4.43	6.14
Ser-Met (z = 0)	-	7.15	5.85	-5.85	-2.02	3.94
Thr-Met (z = 0)	-	7.75	6.17	-6.17	-1.10	3.64
His-Met (z = 0)	98.08 (His)	8.41	6.72	-6.72	-0.94	3.83
Trp-Met (z = 0)	97.10 (Trp)	8.01	6.11	-6.11	-1.14	3.17
Met-Gly (z = 0)	-	8.53	6.33	-6.33	-1.10	3.72
Met-Ala (z = 0)	-	7.91	6.35	-6.35	-0.97	3.66
Met-Val (z = 0)	-	8.44	6.23	-6.23	-1.09	3.66
Met-Leu (z = 0)	-	8.63	6.35	-6.35	-1.11	3.73
Met-Ile (z = 0)	-	8.40	6.23	-6.23	-1.04	3.63
Met-Phe (z = 0)	-	7.81	6.33	-6.33	-0.89	3.61
Met-Pro (z = 0)	-	8.32	6.41	-6.41	-0.72	3.56
Met-Cys (z = 0)	81.44 (Cys)	7.90	6.39	-6.39	-1.23	3.81
Met-Asn (z = 0)	-	8.60	6.41	-6.41	-1.20	3.80
Met-Asp(z = -1)	-	4.15	2.56	-2.56	-1.62	0.47
Met-Gln (z = 0)	-	7.48	6.35	-6.35	-1.88	4.12
Met-Glu (z = -1)	-	4.11	2.59	-2.59	-1.54	0.53
Met-Lys (z = 1)	-	10.39	9.33	-9.33	-4.44	6.88
Met-Arg(z = 1)	-	9.30	8.66	-8.66	-3.96	6.31
Met-Ser (z = 0)	-	8.53	6.42	-6.42	-1.24	3.83
Met-Thr (z = 0)	-	7.58	6.26	-6.26	-1.87	4.07
Met-His (z = 0)	90.22 (His)	8.13	6.21	-6.21	-1.36	3.78
Met-Trp (z = 0)	86.89 (Trp)	7.08	5.50	-5.50	-0.83	3.63

Table S4. Thermodynamic and energy characteristics of the tyrosine-containing dipeptides in the gas phase (298 K).

Compound	EBD, kCal/mol	IPe, eV	IPo, eV	E _{HOMO} , eV	E _{LUMO} , eV	χ , eV
Gly-Tyr (z = 0)	81.94	7.84	6.03	-6.03	-1.11	3.57
Ala-Tyr (z = 0)	81.89	7.48	6.01	-6.01	-0.88	3.45
Val-Tyr (z = 0)	81.43	7.37	5.89	-5.89	-1.07	3.48
Leu-Tyr (z = 0)	81.74	7.69	6.00	-6.00	-0.88	3.44
Ile-Tyr (z = 0)	81.36	7.33	5.88	-5.88	-1.03	3.46
Phe-Tyr (z = 0)	81.86	7.50	6.00	-6.00	-1.11	3.56
Pro-Tyr (z = 0)	81.69	7.40	6.00	-6.00	-1.08	3.54
Met-Tyr (z = 0)	80.75	6.38	5.41	-5.41	-1.78	3.59
Cys-Tyr (z = 0) Cys/Tyr	99.6/75.78	6.86	5.89	-5.89	-1.26	3.60
Asn-Tyr (z = 0)	79.95	7.26	6.03	-6.03	-1.06	3.55
Asp-Tyr (z = -1)	76.46	4.02	2.82	-2.82	1.54	0.64
Gln-Tyr (z = 0)	81.41	7.30	5.99	-5.99	-1.11	3.55
Glu-Tyr (z = -1)	76.24	4.08	2.82	-2.82	1.49	0.67
Lys-Tyr (z = 1)	86.13	9.53	8.16	-8.16	-1.60	4.88
Arg-Tyr (z = 1)	85.60	8.73	8.01	-8.01	-1.19	4.60
Ser-Tyr (z = 0)	80.65	6.36	5.28	-5.28	-1.88	3.58
Thr-Tyr (z = 0)	80.66	6.27	5.27	-5.27	-1.78	3.52
His-Tyr (z = 0) His/Tyr	-/81.89	7.51	6.02	-6.02	-1.07	3.55
Trp-Tyr (z = 0) Trp/Tyr	84.20/82.30	7.55	6.19	-6.19	-1.08	3.63
Tyr-Tyr (z = 0) N-Tyr/C-Tyr	89.21/81.79	7.41	6.00	-6.00	-0.92	3.46
Tyr-Gly (z = 0)	83.66	8.21	6.59	-6.59	-0.93	3.76
Tyr-Ala (z = 0)	83.63	8.13	6.56	-6.56	-0.90	3.73
Tyr-Val (z = 0)	80.69	8.11	6.53	-6.53	-0.88	3.70
Tyr-Leu (z = 0)	81.00	8.10	6.58	-6.58	-0.91	3.75
Tyr-Ile (z = 0)	80.64	8.03	6.54	-6.54	-0.88	3.71
Tyr-Phe (z = 0)	89.00	7.72	6.57	-6.57	-0.93	3.75
Tyr-Pro (z = 0)	83.32	8.02	6.53	-6.53	-0.92	3.73
Tyr-Cys (z = 0) Tyr/Cys	83.29/83.76	7.82	6.49	-6.49	-0.95	3.72
Tyr-Asn (z = 0)	87.95	8.14	6.99	-6.99	-0.89	3.44
Tyr-Asp(z = -1)	78.98	4.35	2.85	-2.85	1.60	0.63
Tyr-Gln (z = 0)	80.84	8.12	6.49	-6.49	-0.85	3.67
Tyr-Glu (z = -1)	76.68	4.62	2.81	-2.81	1.68	0.57
Tyr-Lys (z = 1)	86.85	10.78	8.40	-8.40	-4.17	6.28
Tyr-Arg(z = 1)	86.70	9.09	8.49	-8.49	-4.26	6.38
Tyr-Ser (z = 0)	79.56	8.21	6.48	-6.48	-0.90	3.69
Tyr-Thr (z = 0)	83.08	7.80	6.26	-6.26	-0.93	3.59
Tyr-His (z = 0) Tyr/His	84.78/82.68	7.32	6.01	-6.01	-1.17	3.59
Tyr-Trp (z = 0) Tyr/Trp	78.34/80.22	6.99	5.43	-5.43	-0.89	3.16
Tyr-Met (z = 0)	83.98	7.42	6.23	-6.23	-0.94	3.58