Supporting Information for

Non-Covalent Complexes of the Peptide Fragment Gly-Asn-Asn-Gln-Gln-Asn-Tyr in the Gas-Phase. Photodissociative Cross-Linking, Born-Oppenheimer Molecular Dynamics, and Ab Initio Computational Binding Study

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Table S1. UVPD-CID-MS^3 spectrum of the (*GNNQQNY$_{NH2}$ – N_2 + GNNQQNY$_{NH2}$ + H)$^+$ complex ***I*** (*m/z* 1739)

Fragment Ion (*m/z*)	Assignment[b]	Rel. Intensity[a]
1722	(1739-NH_3)	0.4
1160	***y***$\boldsymbol{y_4}$B$_5$	0.1
1032	$\boldsymbol{y_4}$B$_4$ / $\boldsymbol{y_3}$B$_5$	0.8
1018	$\boldsymbol{y_6}$B$_2$ / $\boldsymbol{y_5}$B$_3$ / $\boldsymbol{y_2}$B$_6$	0.3
961	***m***B$_1$ / $\boldsymbol{b_1}$M	0.7
904	[M+H]$^+$	75.9
887	[M-NH_3+H]$^+$	7.9
870	[M-2NH_3+H]$^+$	2.2
836	[***m***+H]$^+$	2.0
819	[***m***-NH_3+H]$^+$	0.3
790	$\boldsymbol{y_1}$B$_5$ / $\boldsymbol{y_4}$B$_2$ / $\boldsymbol{y_5}$B$_1$	0.1
724	B$_6$	1.7
707	B$_6$-NH_3	0.9
662	$\boldsymbol{y_1}$B$_4$ / $\boldsymbol{y_3}$B$_2$	0.1
648	$\boldsymbol{y_2}$B$_3$	0.2
610	B$_5$	0.9
593	B$_5$-NH_3	0.3

[a]Relative to the sum of fragment ion intensities.
[b]Fragment ions indicative of crosslinking in GNNQQNY$_{NH2}$ are highlighted.

Table S2. UVPD-CID-MS^3 spectrum of the (*$GNNQQNY_{OH} - N_2 + GNNQQNY_{OH} + H)^+$ complex ***II*** (*m/z* 1741)

Fragment Ion (*m/z*)	Assignment[b]	
1724	(1741-NH_3)	3.1
1707	(1741-2NH_3)	0.8
1570	$\boldsymbol{y_5}M$	0.2
1560	$\boldsymbol{m}B_6/\boldsymbol{b_6}M$	0.5
1553	$\boldsymbol{y_5}M$-NH_3	0.1
1543	$\boldsymbol{m}B_6/\boldsymbol{b_6}M$-$NH_3$	0.2
1456	$\boldsymbol{y_4}M$	0.1
1446	$\boldsymbol{m}B_5/\boldsymbol{b_5}M$	0.3
1439	$\boldsymbol{y_4}M$-NH_3	0.1
1429	$\boldsymbol{m}B_5/\boldsymbol{b_5}M$-$NH_3$	0.1
1328	$\boldsymbol{y_3}M$	0.1
1318	$\boldsymbol{m}B_4/\boldsymbol{b_4}M$	0.2
1311	$\boldsymbol{y_3}M$-NH_3	0.2
1301	$\boldsymbol{m}B_4/\boldsymbol{b_4}M$-$NH_3$	0.1
1200	$\boldsymbol{y_2}M$	0.3
1190	$\boldsymbol{m}B_3/\boldsymbol{b_3}M$	0.1
1183	$\boldsymbol{y_2}M$-NH_3	0.2
1173	$\boldsymbol{m}B_3/\boldsymbol{b_3}M$-$NH_3$	0.1
1086	$\boldsymbol{y_1}M$	0.2
1076	$\boldsymbol{m}B_2/\boldsymbol{b_2}M$	0.2
1069	$\boldsymbol{y_1}M$-NH_3	0.1
1059	$\boldsymbol{m}B_2/\boldsymbol{b_2}M$ -NH_3	0.1
1019	$\boldsymbol{y_6}B_2$ / $\boldsymbol{y_5}B_3$ / $\boldsymbol{y_2}B_6$	0.1
962	$\boldsymbol{m}B_1$ / $\boldsymbol{b_1}M$	0.5
905	$[M+H]^+$	81.1
888	$[M-NH_3+H]^+$	3.2
871	$[M-2NH_3+H]^+$	0.6
837	$[\boldsymbol{m}+H]^+$	1.7
820	$[\boldsymbol{m}-NH_3+H]^+$	0.1
791	$\boldsymbol{y_5}B_1$ / $\boldsymbol{y_4}B_2$ / $\boldsymbol{y_1}B_5$	0.1
777	$\boldsymbol{y_3}B_3$ / $\boldsymbol{y_2}B_4$	0.1
724	B_6	1.5
707	B_6-NH_3	0.7
690	B_6-2NH_3	0.3
649	$\boldsymbol{y_2}B_3$	0.1
639	$\boldsymbol{b_3}B_3$	0.1
610	B_5	1.2
593	B_5-NH_3	0.4

[a]Relative to the sum of fragment ion intensities.
[b]Fragment ions indicative of crosslinking in $GNNQQNY_{OH}$ are highlighted.

Table S3. UVPD-CID-MS^3 spectrum of the $(*GNNQQNY_{OH} – N_2 + GNNQQNY_{NH2} + H)^+$ complex ***III*** (*m/z* 1740)

Fragment Ion (*m/z*)	Assignment	Rel. Intensity[a]
1723	$(1740-NH_3)$	0.4
961	***m***B_1	0.8
905	$[M+H]^+$	87.2
888	$[M-NH_3+H]^+$	3.2
871	$[M-2NH_3+H]^+$	0.6
836	$[m+H]^+$	2.5
819	$[m-NH_3+H]^+$	0.3
802	$[m-2NH_3+H]^+$	0.6
724	B_6	1.6
707	B_6-NH_3	0.7
690	B_6-2NH_3	0.3
610	B_5	1.2
593	B_5-NH_3	0.4

[a]Relative to the sum of fragment ion intensities.

Table S4. UVPD-CID-MS^3 spectrum of the (*GNNQQNY$_{NH2}$ – N_2 + GNNQQNY$_{OH}$ + H)$^+$ complex ***IV*** (*m/z* 1740)

Fragment Ion (*m/z*)	Assignment[b]	Rel. Intensity[a]
1723	(1740-NH_3)	5.0
1706	(1740-2NH_3)	0.1
1689	(1740-3NH_3)	0.4
1569	$\boldsymbol{y_5}$M	0.2
1560	***m***B_6	0.4
1552	$\boldsymbol{y_5}$M-NH_3	0.1
1543	***m***B_6-NH_3	0.2
1455	$\boldsymbol{y_4}$M	0.1
1446	***m***B_5	0.4
1438	$\boldsymbol{y_4}$M-NH_3	0.1
1429	***m***B_5-NH_3	0.1
1412	***m***B_5-2NH_3	0.1
1327	$\boldsymbol{y_3}$M	0.1
1318	***m***B_4	0.3
1310	$\boldsymbol{y_3}$M-NH_3	0.2
1301	***m***B_4-NH_3	0.1
1293	$\boldsymbol{y_3}$M-2NH_3	0.1
1284	***m***B_4-2NH_3	0.1
1199	$\boldsymbol{y_2}$M	0.3
1190	***m***B_3	0.2
1182	$\boldsymbol{y_2}$M-NH_3	0.3
1173	***m***B_3-NH_3	0.1
1085	$\boldsymbol{y_1}$M	0.2
1076	***m***B_2	0.3
1067	$\boldsymbol{y_1}$M-H_2O	0.3
962	***m***B_1	0.3
904	$[M+H]^+$	72.3
887	$[M-NH_3+H]^+$	7.2
870	$[M-2NH_3+H]^+$	2.4
853	$[M-3NH_3+H]^+$	0.9
837	$[\boldsymbol{m}+H]^+$	1.2
820	$[\boldsymbol{m}-NH_3+H]^+$	0.1
724	B_6	1.7
707	B_6-NH_3	0.9
690	B_6-2NH_3	0.3
610	B_5	0.9
593	B_5-NH_3	0.4

[a]Relative to the sum of fragment ion intensities.
[b]Fragment ions indicative of crosslinking in GNNQQNY$_{OH}$ are highlighted.

Table S5. Table of logical combinations of B-ions from the photo-labeled monomer *GNNQQNY$_{NH2}$ and the ***b***- and ***y***-ions from the PAGGYYQNY$_{NH2}$ target monomer.

	$\boldsymbol{b_1}$	$\boldsymbol{b_2}$	$\boldsymbol{b_3}$	$\boldsymbol{b_4}$	$\boldsymbol{b_5}$	$\boldsymbol{b_6}$	$\boldsymbol{b_7}$	$\boldsymbol{b_8}$
	98.1	169.1	226.1	283.1	446.2	609.3	737.3	851.4
B_1	$\boldsymbol{b_1}B_1$	$\boldsymbol{b_2}B_1$	$\boldsymbol{b_3}B_1$	$\boldsymbol{b_4}B_1$	$\boldsymbol{b_5}B_1$	$\boldsymbol{b_6}B_1$	$\boldsymbol{b_7}B_1$	$\boldsymbol{b_8}B_1$
126.1	223.1	294.2	351.2	408.2	571.3	734.4	862.4	976.5
B_2	$\boldsymbol{b_1}B_2$	$\boldsymbol{b_2}B_2$	$\boldsymbol{b_3}B_2$	$\boldsymbol{b_4}B_2$	$\boldsymbol{b_5}B_2$	$\boldsymbol{b_6}B_2$	$\boldsymbol{b_7}B_2$	$\boldsymbol{b_8}B_2$
240.1	337.2	408.2	465.2	522.3	685.3	848.4	976.4	1090.5
B_3	$\boldsymbol{b_1}B_3$	$\boldsymbol{b_2}B_3$	$\boldsymbol{b_3}B_3$	$\boldsymbol{b_4}B_3$	$\boldsymbol{b_5}B_3$	$\boldsymbol{b_6}B_3$	$\boldsymbol{b_7}B_3$	$\boldsymbol{b_8}B_3$
354.2	451.2	522.3	579.3	636.3	799.4	962.4	1090.5	1204.5
B_4	$\boldsymbol{b_1}B_4$	$\boldsymbol{b_2}B_4$	$\boldsymbol{b_3}B_4$	$\boldsymbol{b_4}B_4$	$\boldsymbol{b_5}B_4$	$\boldsymbol{b_6}B_4$	$\boldsymbol{b_7}B_4$	$\boldsymbol{b_8}B_4$
482.2	579.3	650.3	707.3	764.4	927.4	1090.5	1218.6	1332.6
B_5	$\boldsymbol{b_1}B_5$	$\boldsymbol{b_2}B_5$	$\boldsymbol{b_3}B_5$	$\boldsymbol{b_4}B_5$	$\boldsymbol{b_5}B_5$	$\boldsymbol{b_6}B_5$	$\boldsymbol{b_7}B_5$	$\boldsymbol{b_8}B_5$
610.3	707.3	778.4	835.4	892.4	1055.5	1218.6	1346.6	1460.7
B_6	$\boldsymbol{b_1}B_6$	$\boldsymbol{b_2}B_6$	$\boldsymbol{b_3}B_6$	$\boldsymbol{b_4}B_6$	$\boldsymbol{b_5}B_6$	$\boldsymbol{b_6}B_6$	$\boldsymbol{b_7}B_6$	$\boldsymbol{b_8}B_6$
724.3	821.4	892.4	949.4	1006.5	1169.5	1332.6	1460.7	1574.7
M	$\boldsymbol{b_1}M$	$\boldsymbol{b_2}M$	$\boldsymbol{b_3}M$	$\boldsymbol{b_4}M$	$\boldsymbol{b_5}M$	$\boldsymbol{b_6}M$	$\boldsymbol{b_7}M$	$\boldsymbol{b_8}M$
904.4	1001.5	1072.5	1129.5	1186.6	1349.6	1512.7	1640.7	1754.8

	$\boldsymbol{y_1}$	$\boldsymbol{y_2}$	$\boldsymbol{y_3}$	$\boldsymbol{y_4}$	$\boldsymbol{y_5}$	$\boldsymbol{y_6}$	$\boldsymbol{y_7}$	$\boldsymbol{y_8}$
	181.1	295.1	423.2	586.3	749.3	806.3	863.4	934.4
B_1	$\boldsymbol{y_1}B_1$	$\boldsymbol{y_2}B_1$	$\boldsymbol{y_3}B_1$	$\boldsymbol{y_4}B_1$	$\boldsymbol{y_5}B_1$	$\boldsymbol{y_6}B_1$	$\boldsymbol{y_7}B_1$	$\boldsymbol{y_8}B_1$
126.1	306.2	420.2	548.3	711.3	874.4	931.4	988.5	1059.5
B_2	$\boldsymbol{y_1}B_2$	$\boldsymbol{y_2}B_2$	$\boldsymbol{y_3}B_2$	$\boldsymbol{y_4}B_2$	$\boldsymbol{y_5}B_2$	$\boldsymbol{y_6}B_2$	$\boldsymbol{y_7}B_2$	$\boldsymbol{y_8}B_2$
240.1	420.2	534.3	662.3	825.4	988.5	1045.5	1102.5	1173.5
B_3	$\boldsymbol{y_1}B_3$	$\boldsymbol{y_2}B_3$	$\boldsymbol{y_3}B_3$	$\boldsymbol{y_4}B_3$	$\boldsymbol{y_5}B_3$	$\boldsymbol{y_6}B_3$	$\boldsymbol{y_7}B_3$	$\boldsymbol{y_8}B_3$
354.2	534.3	648.3	776.4	939.4	1102.5	1159.5	1216.5	1287.6
B_4	$\boldsymbol{y_1}B_4$	$\boldsymbol{y_2}B_4$	$\boldsymbol{y_3}B_4$	$\boldsymbol{y_4}B_4$	$\boldsymbol{y_5}B_4$	$\boldsymbol{y_6}B_4$	$\boldsymbol{y_7}B_4$	$\boldsymbol{y_8}B_4$
482.2	662.3	776.4	904.4	1067.4	1230.6	1287.6	1344.6	1415.6
B_5	$\boldsymbol{y_1}B_5$	$\boldsymbol{y_2}B_5$	$\boldsymbol{y_3}B_5$	$\boldsymbol{y_4}B_5$	$\boldsymbol{y_5}B_5$	$\boldsymbol{y_6}B_5$	$\boldsymbol{y_7}B_5$	$\boldsymbol{y_8}B_5$
610.3	790.4	904.4	1032.5	1195.5	1358.6	1415.6	1472.7	1543.7
B_6	$\boldsymbol{y_1}B_6$	$\boldsymbol{y_2}B_6$	$\boldsymbol{y_3}B_6$	$\boldsymbol{y_4}B_6$	$\boldsymbol{y_5}B_6$	$\boldsymbol{y_6}B_6$	$\boldsymbol{y_7}B_6$	$\boldsymbol{y_8}B_6$
724.3	904.4	1018.5	1146.5	1309.6	1472.7	1529.7	1586.7	1657.7
M	$\boldsymbol{y_1}M$	$\boldsymbol{y_2}M$	$\boldsymbol{y_3}M$	$\boldsymbol{y_4}M$	$\boldsymbol{y_5}M$	$\boldsymbol{y_6}M$	$\boldsymbol{y_7}M$	$\boldsymbol{y_8}M$
904.4	1084.5	1198.6	1326.6	1489.7	1652.7	1709.8	1766.8	1837.8

Table S6. UVPD-CID-MS^3 spectrum of the (*GNNQQNY$_{NH2}$ – N_2 + PAGGYYQNY$_{NH2}$ + H)$^+$ complex (*m/z* 1934).

Fragment Ion (*m/z*)	Assignment[b]	Rel. Intensity[a]
1918	(1934-NH_3)	0.9
1901	(1934-2NH_3)	0.4
1514	--	0.3
1480	--	0.3
1098	--	2.1
1053	--	1.9
1031	[***n***+H]$^+$	53.9
1014	[***n***-NH_3+H]$^+$	2.0
972	--	5.8
904	[M+H]$^+$	25.3
887	[M-NH_3+H]$^+$	2.8
870	[M-2NH_3+H]$^+$	0.7
851	$\boldsymbol{b_8}$	0.5
834	$\boldsymbol{b_8\text{-}NH_3}$	0.8
737	$\boldsymbol{b_7}$	0.7
724	B_6	0.6
707	B_6-NH_3	0.3
610	B_5	0.3
609	$\boldsymbol{b_6}$	0.2

[a]Relative to the sum of fragment ion intensities.
[b]Ions that were not able to be logically assigned are denoted "--"

Table S7. Table of logical combinations of B-ions from the photo-labeled monomer *GNNQQNY-NH_2 and the ***b***- and ***y***-ions from the PQGGYQQYN$_{NH2}$ target monomer.

	b_1 98.1	b_2 226.1	b_3 283.1	b_4 340.2	b_5 503.2	b_6 631.3	b_7 759.3	b_8 922.4
B_1 126.1	b_1B_1 223.1	b_2B_1 351.2	b_3B_1 408.2	b_4B_1 465.2	b_5B_1 628.3	b_6B_1 756.4	b_7B_1 884.4	b_8B_1 1047.5
B_2 240.1	b_1B_2 337.2	b_2B_2 465.2	b_3B_2 522.3	b_4B_2 579.3	b_5B_2 742.4	b_6B_2 870.4	b_7B_2 998.5	b_8B_2 1161.5
B_3 354.2	b_1B_3 451.2	b_2B_3 579.3	b_3B_3 636.3	b_4B_3 693.3	b_5B_3 856.4	b_6B_3 984.5	b_7B_3 1112.5	b_8B_3 1275.6
B_4 482.2	b_1B_4 579.3	b_2B_4 707.3	b_3B_4 764.4	b_4B_4 821.4	b_5B_4 984.5	b_6B_4 1112.5	b_7B_4 1240.6	b_8B_4 1403.6
B_5 610.3	b_1B_5 707.3	b_2B_5 835.4	b_3B_5 892.4	b_4B_5 949.4	b_5B_5 1112.5	b_6B_5 1240.6	b_7B_5 1368.6	b_8B_5 1531.7
B_6 724.3	b_1B_6 821.4	b_2B_6 949.4	b_3B_6 1006.5	b_4B_6 1063.5	b_5B_6 1226.6	b_6B_6 1354.6	b_7B_6 1482.7	b_8B_6 1645.7
M 904.4	b_1M 1001.5	b_2M 1129.5	b_3M 1186.6	b_4M 1243.6	b_5M 1406.6	b_6M 1534.7	b_7M 1662.8	b_8M 1825.8

	y_1 132.1	y_2 295.1	y_3 423.2	y_4 551.3	y_5 714.3	y_6 771.3	y_7 828.4	y_8 956.4
B_1 126.1	y_1B_1 257.2	y_2B_1 420.2	y_3B_1 548.3	y_4B_1 676.3	y_5B_1 839.4	y_6B_1 896.4	y_7B_1 953.4	y_8B_1 1081.5
B_2 240.1	y_1B_2 371.2	y_2B_2 534.3	y_3B_2 662.3	y_4B_2 790.4	y_5B_2 953.4	y_6B_2 1010.5	y_7B_2 1067.5	y_8B_2 1195.5
B_3 354.2	y_1B_3 485.2	y_2B_3 648.3	y_3B_3 776.4	y_4B_3 904.4	y_5B_3 1067.5	y_6B_3 1124.5	y_7B_3 1181.5	y_8B_3 1309.6
B_4 482.2	y_1B_4 613.3	y_2B_4 776.4	y_3B_4 904.4	y_4B_4 1032.4	y_5B_4 1195.5	y_6B_4 1252.6	y_7B_4 1309.6	y_8B_4 1437.7
B_5 610.3	y_1B_5 741.4	y_2B_5 904.4	y_3B_5 1032.5	y_4B_5 1160.5	y_5B_5 1323.6	y_6B_5 1380.6	y_7B_5 1437.7	y_8B_5 1565.7
B_6 724.3	y_1B_6 855.4	y_2B_6 1018.5	y_3B_6 1146.5	y_4B_6 1274.6	y_5B_6 1437.7	y_6B_6 1494.7	y_7B_6 1551.7	y_8B_6 1679.8
M 904.4	y_1M 1035.5	y_2M 1198.6	y_3M 1326.6	y_4M 1454.7	y_5M 1617.7	y_6M 1674.8	y_7M 1731.8	y_8M 1859.8

Table S8. UVPD-CID-MS^3 spectrum of the (*GNNQQNY$_{NH2}$ – N_2 + PQGGYQQYN$_{NH2}$ + H)$^+$ complex (*m/z* 1956).

Fragment Ion (*m/z*)	Assignment[b]	Rel. Intensity[a]
1939	(1956-NH_3)	1.0
1922	(1956-2NH_3)	0.2
1899	--	0.7
1503	--	0.2
1439	--	0.4
1053	[***p***+H]$^+$	72.1
1036	[***p***-NH_3+H]$^+$	2.0
994	--	3.2
926	[M+Na]$^+$	7.9
904	[M+H]$^+$	8.5
887	[M-NH_3+H]$^+$	1.0
870	[M-2NH_3+H]$^+$	0.3
828	$\boldsymbol{y_7}$	0.4
759	$\boldsymbol{b_7}$	0.4
742	B_6	0.2
631	$\boldsymbol{b_6}$	0.3
614	$\boldsymbol{b_6}$-NH_3	0.1
610	B_5	0.1

[a]Relative to the sum of fragment ion intensities.
[b]Ions that were not able to be logically assigned are denoted "--"

Table S9. Relative Energies of $(GNNQQNY_{NH2} + *GNNQQNY_{NH2} + H)^+$ Ion Complexes.

Complex	Relative Energy[a] ($kJ\ mol^{-1}$)			
	B3LYP/ 6-31G(d,p)	ωB97XD/6-31+G(d,p)		
1	0 (0.0)[b]	0 (0.0)	0[c]	0[c]
2	15 (2.3)	40 (27)	28[c] (15)	27[d] (14)
3	53 (29)	76 (52)	50[e] (26)	49[f] (25)
4	103 (78)	95 (70)	58[e] (33)	58[f] (33)
5	98 (84)	104 (90)	97[e] (83)	96[f] (82)
6	49 (17)	124 (92)	92[e] (59)	91[f] (59)
7	108 (77)	121 (93)	101[e] (72)	100[f] (71)
8	51 (16)	147 (113)	81[e] (47)	83[f] (49)
9	84 (66)	138 (120)	129[e] (111)	128[f] (110)
1–N_2 → **10** + **11**	90	262 (170) 218[g] (126)	103[g] (12)	

[a]Including zero-point vibrational energies and referring to 0 K.
[b]Values in parentheses are the relative free energies at 310 K.
[c]Including solvation energies for fully optimized structures in the water polarizable dielectric .
[d]Including solvation energies for fully optimized structures in the methanol polarizable dielectric.
[e]Including solvation energies in the water polarizable dielectric for gas-phase structures.
[f]Including solvation energies in the methanol polarizable dielectric for gas-phase structures.
[g]Including counterpoise energy corrections of the basis set superposition error.

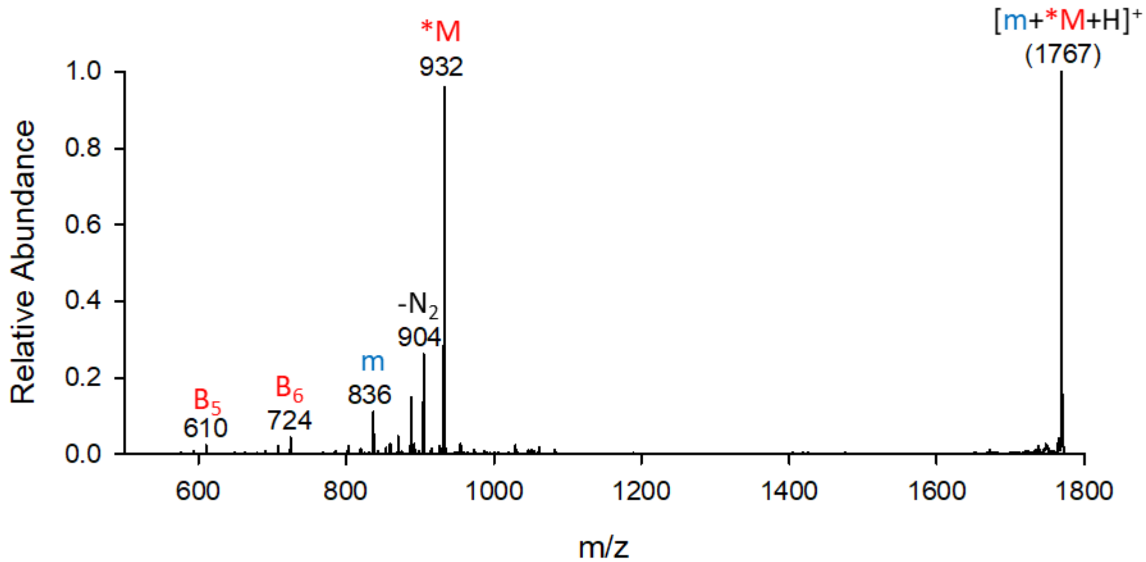

Figure S1. CID-MS^2 of (*GNNQQNY$_{NH2}$ + GNNQQNY$_{NH2}$ + H)$^+$ ion dimer complex.

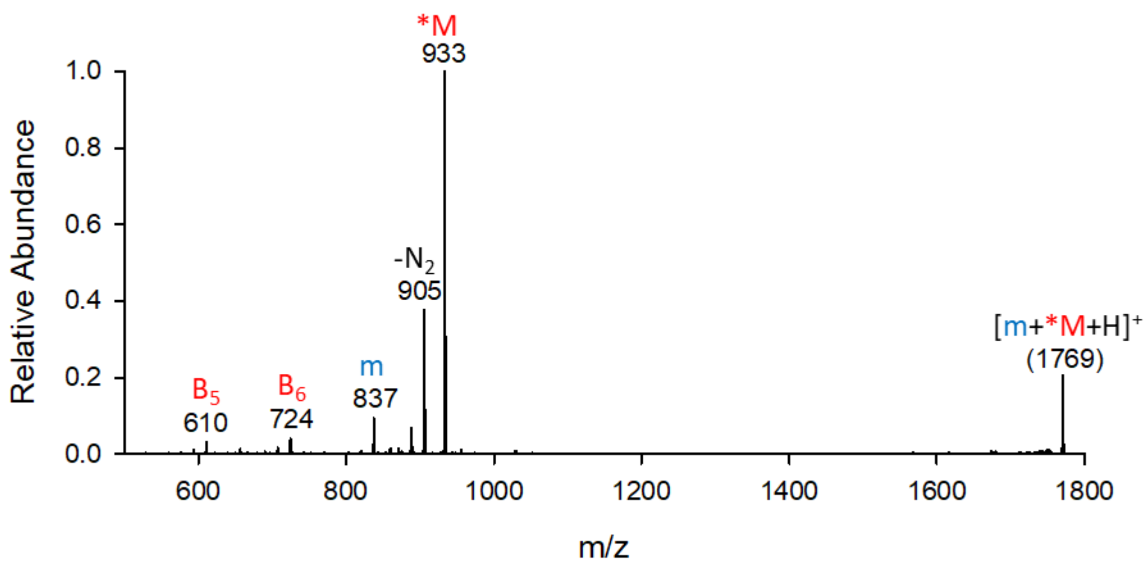

Figure S2. CID-MS^2 of [*GNNQQNY$_{OH}$ + GNNQQNY$_{OH}$ + H]$^+$ ion dimer complex.

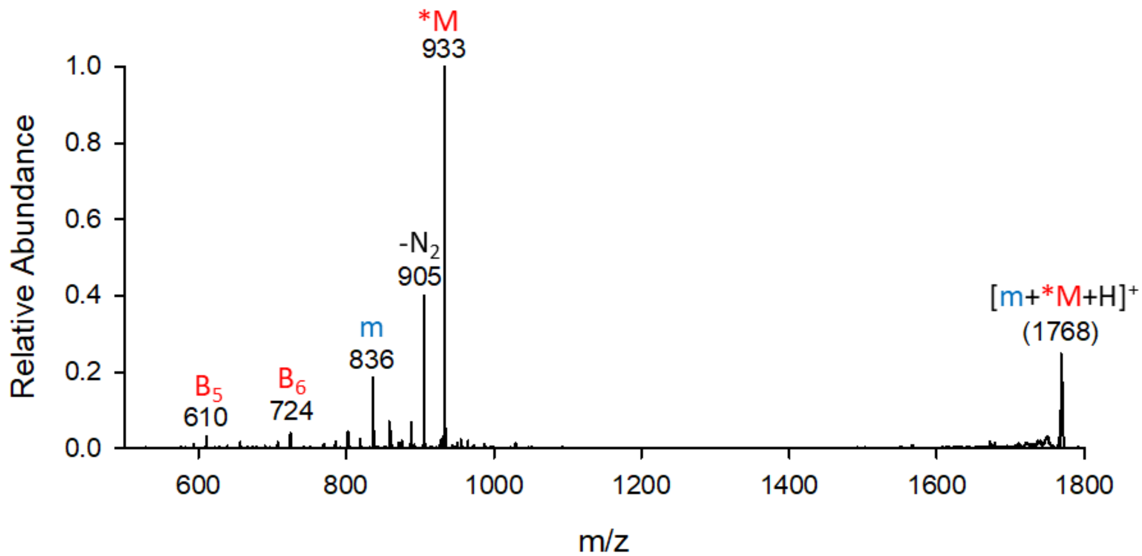

Figure S3. CID-MS^2 of [*GNNQQNY$_{OH}$ + GNNQQNY$_{NH2}$ + H]$^+$ ion dimer complex.

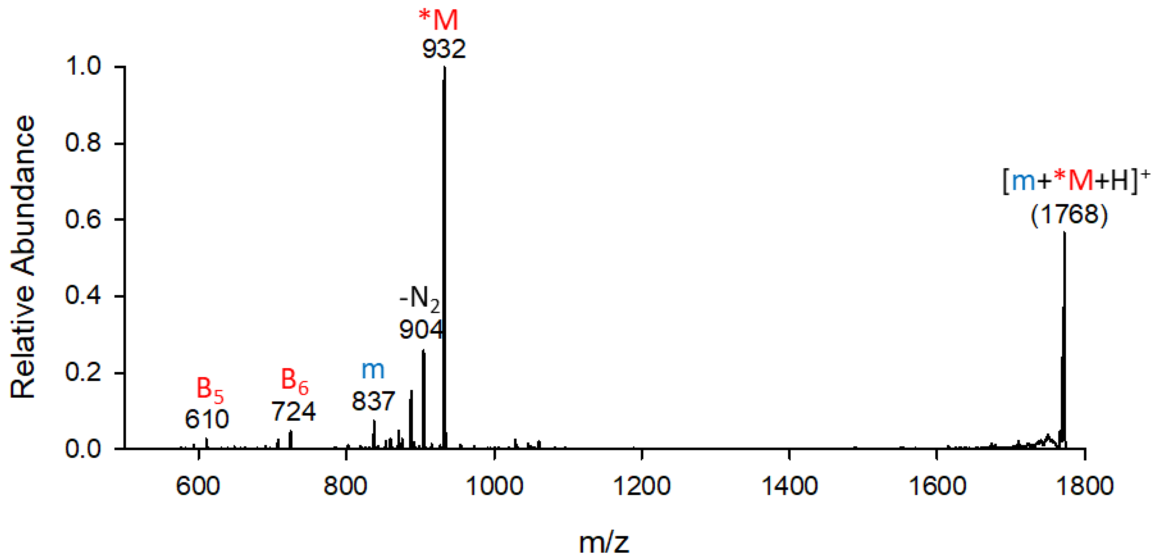

Figure S4. CID-MS^2 of [*GNNQQNY$_{NH2}$ + GNNQQNY$_{OH}$ + H]$^+$ ion dimer complex.

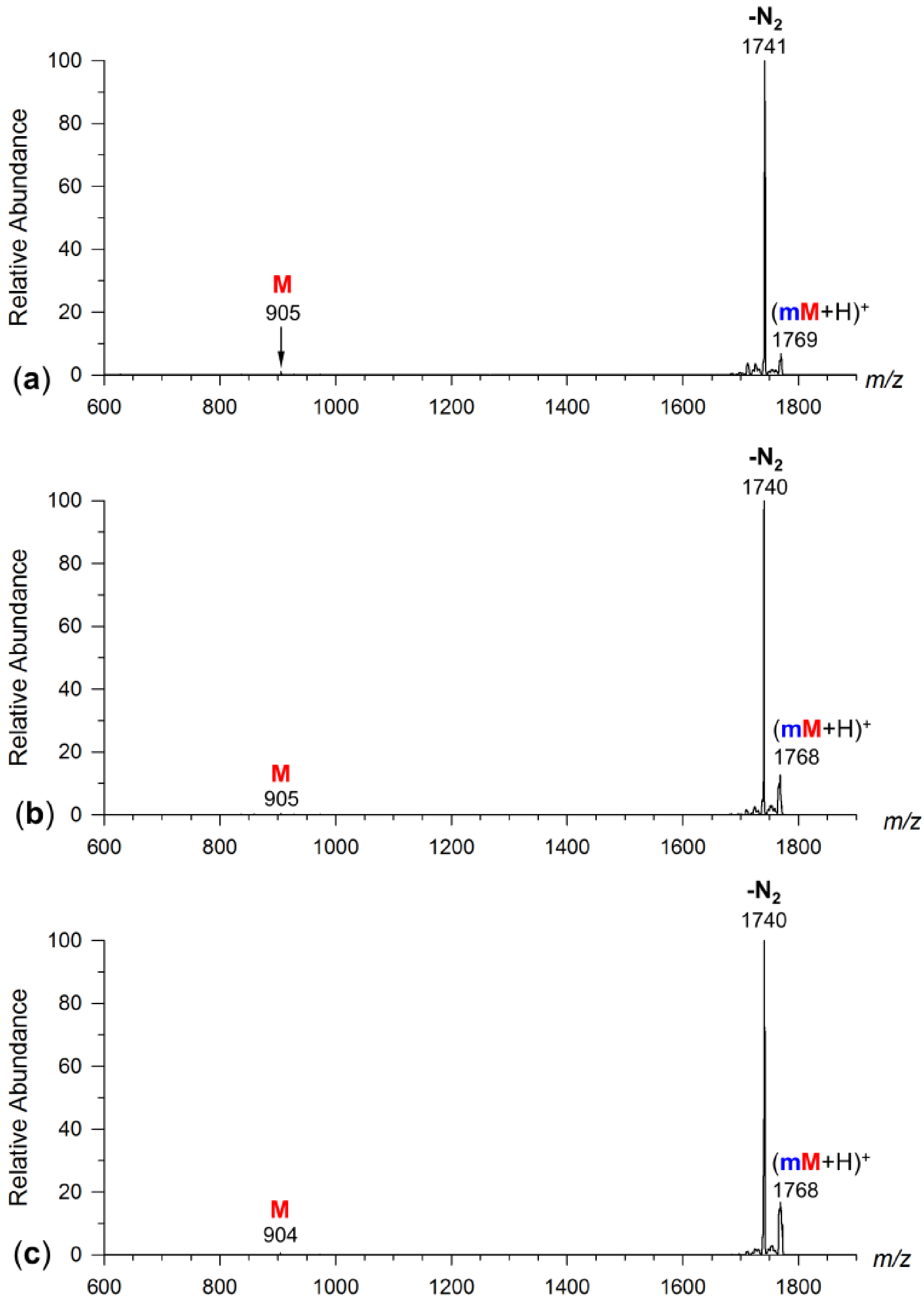

Figure S5. UVPD-MS2 of (a) complex ***II***, (GNNQQNY$_{OH}$ + *GNNQQNY$_{OH}$ + H)$^+$, *m/z* 1769; (b) complex ***III***, (GNNQQNY$_{NH2}$ + *GNNQQNY$_{OH}$ + H)$^+$, *m/z* 1768; (c) complex ***IV***, (GNNQQNY$_{OH}$ + *GNNQQNY$_{NH2}$ + H)$^+$, *m/z* 1768.

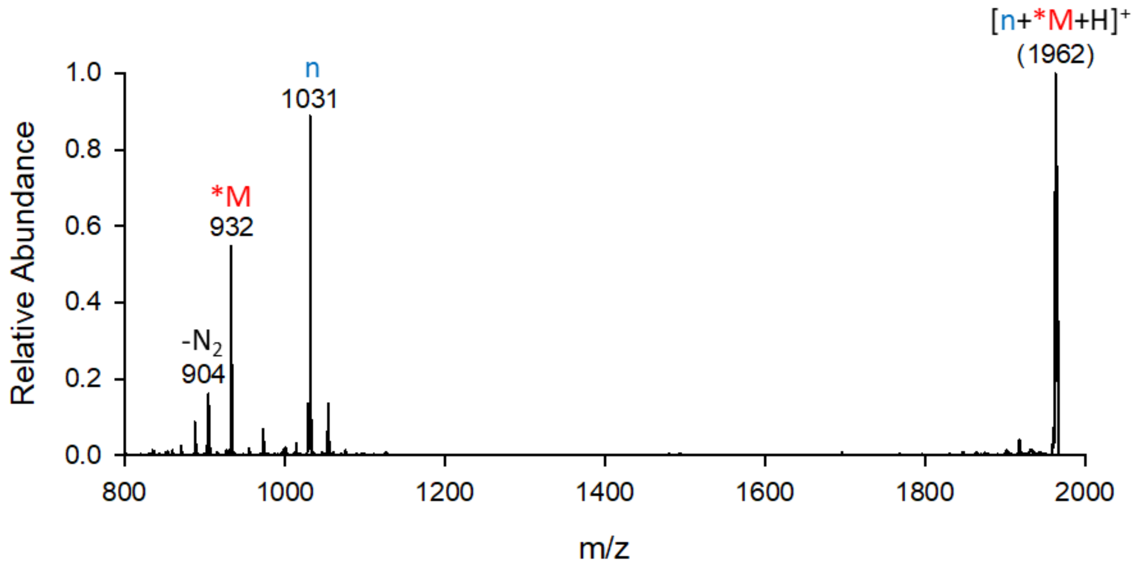

Figure S6. CID-MS^2 of [*GNNQQNY$_{NH2}$ + PAGGYYQNY$_{NH2}$ + H]$^+$ ion dimer complex.

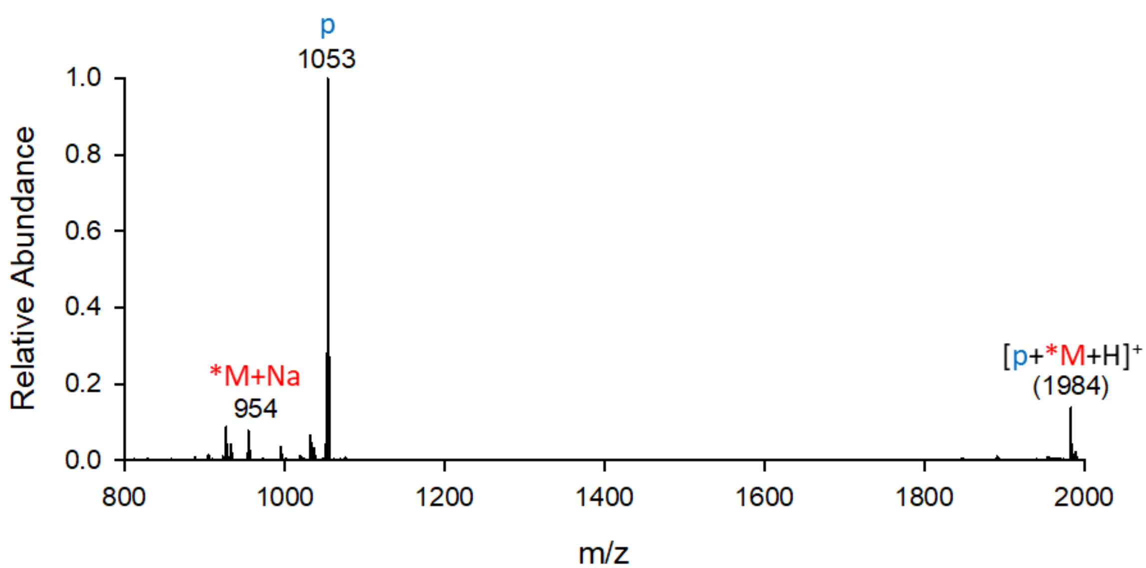

Figure S7. CID-MS^2 of [*GNNQQNY$_{NH2}$ + PQGGYQQYN$_{NH2}$ + H]$^+$ ion dimer complex.

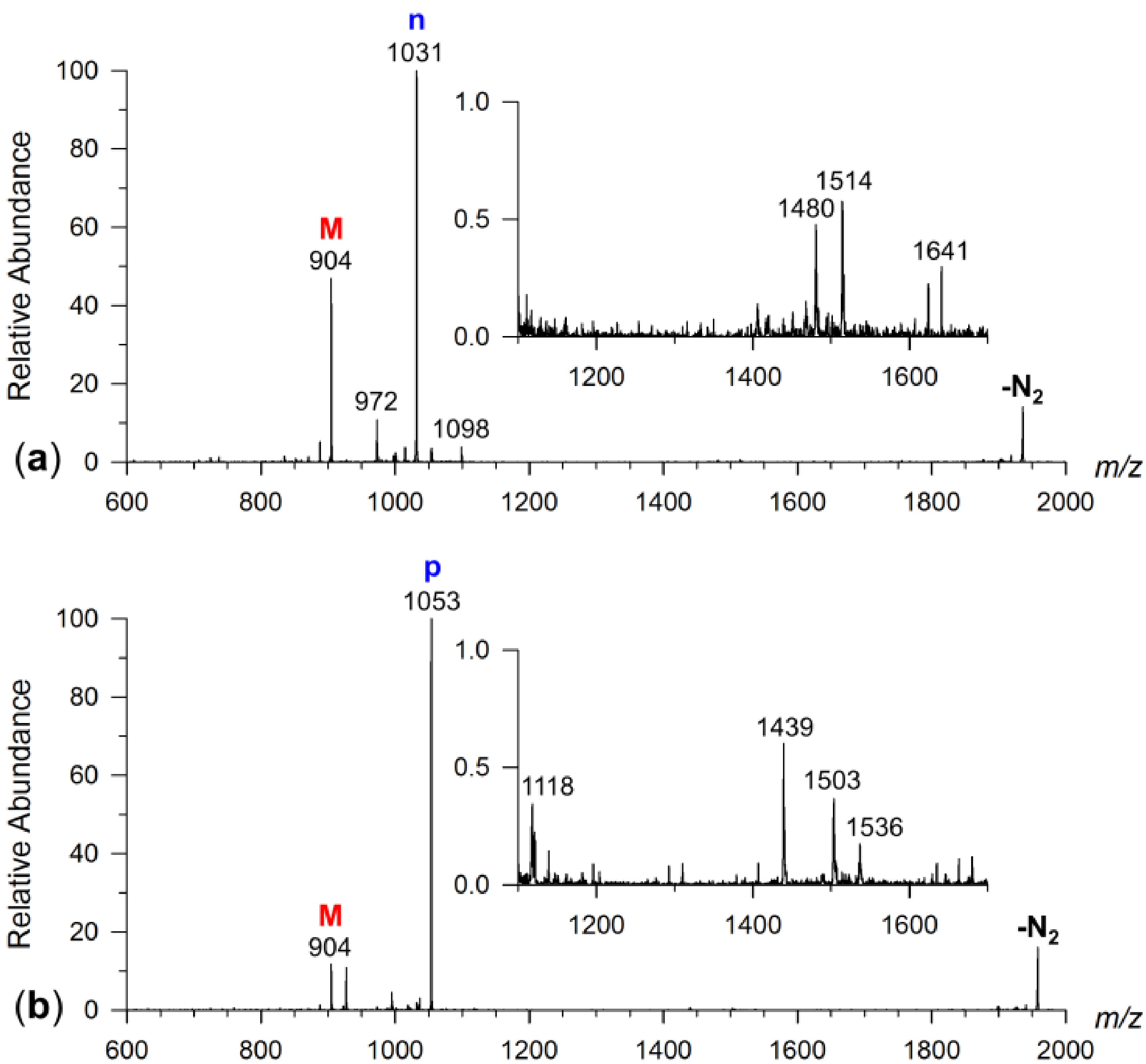

Figure S8. CID-MS[3] of photoproduct ions (a) $(nM–N_2+H)^+$, *m/z* 1934; (b) $(pM–N_2+H)^+$, *m/z* 1956.

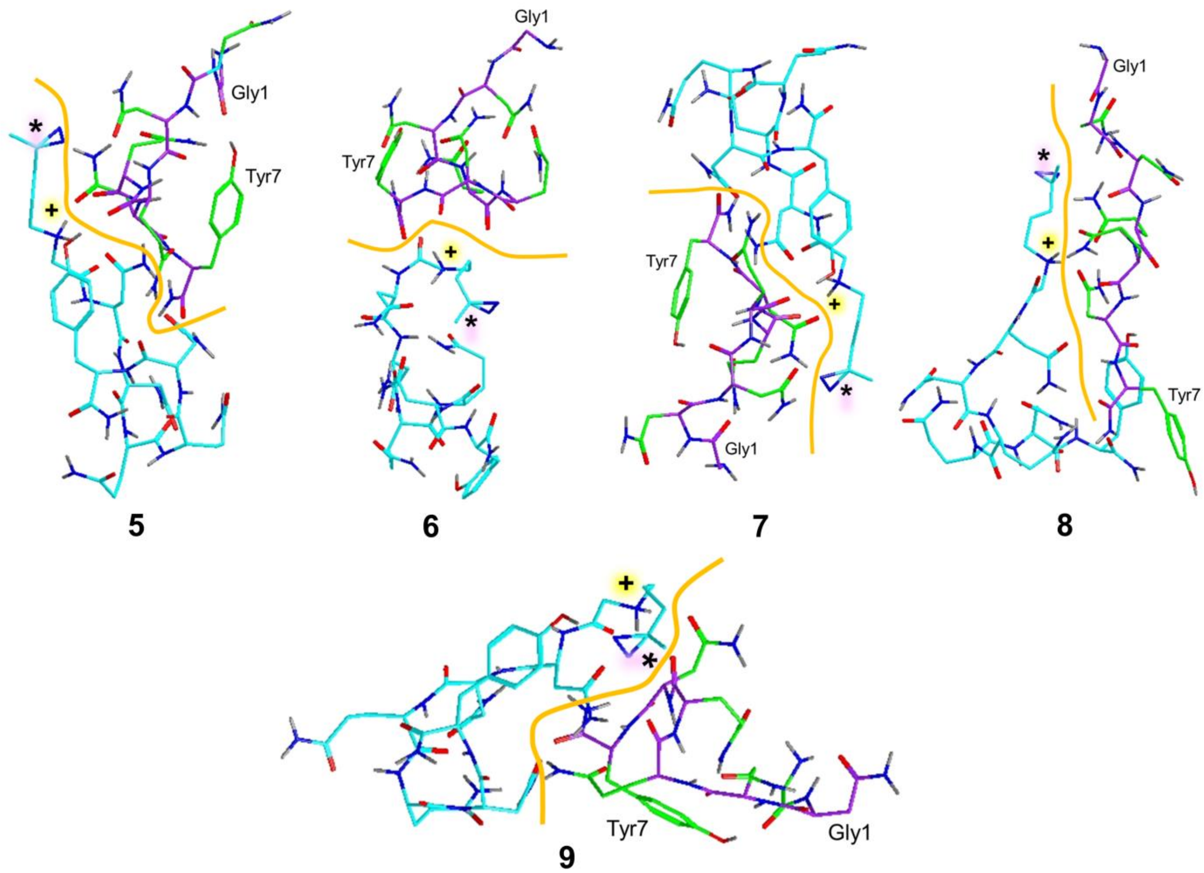

Figure S9. ωB97XD/6-31+G(d,p) optimized structures of complexes **5-9**. Atom color coding as in Figure 6 of the main text.

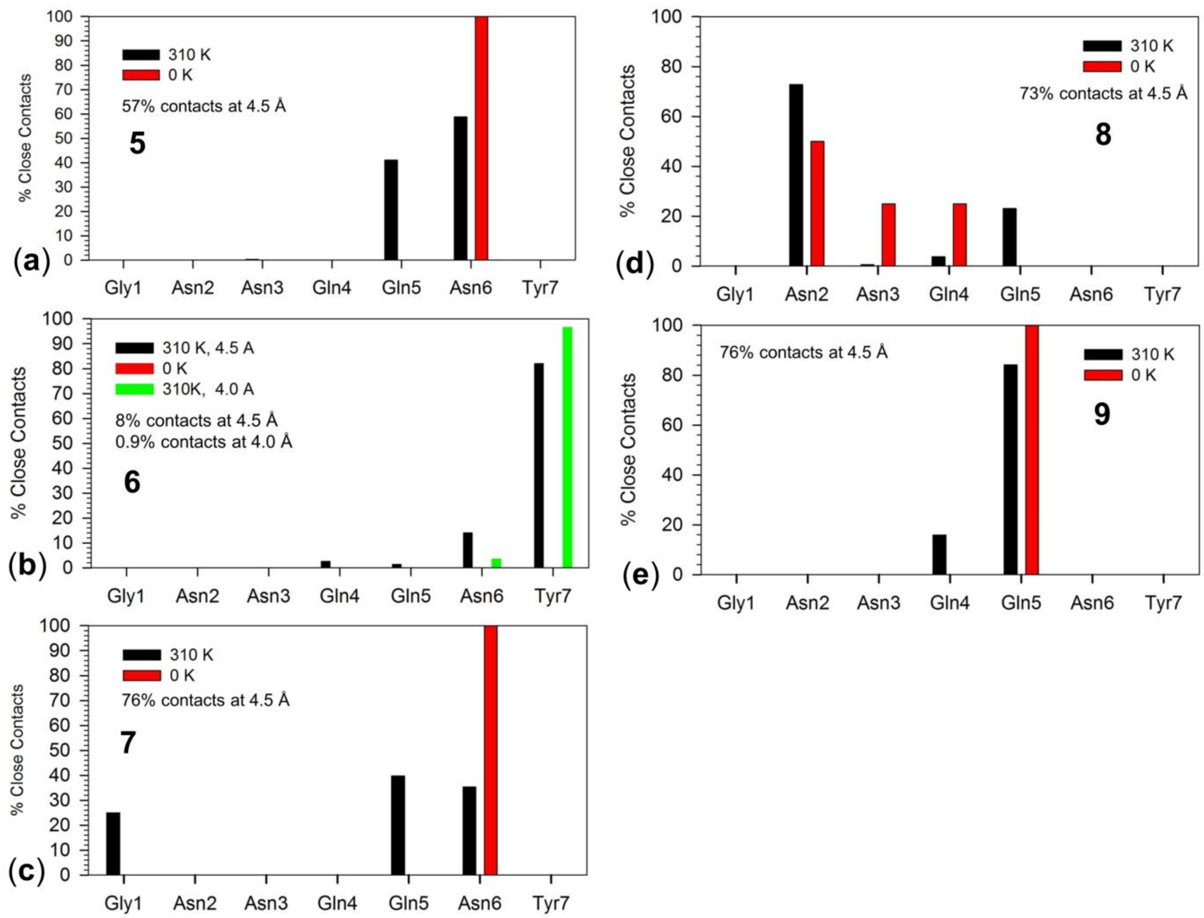

Figure S10. Close contacts between the diazirine carbon and the X—H (X = C, N, O) bonds of $GNNQQNY_{NH2}$ in conformers **5** to **9** in the 100 ps trajectories. Red bars indicate close contacts at 4.5 Å in the optimized structures. Black and green bars indicate close contacts at 4.5 and 4.0 Å, respectively, as a result of 310 K thermal motion.

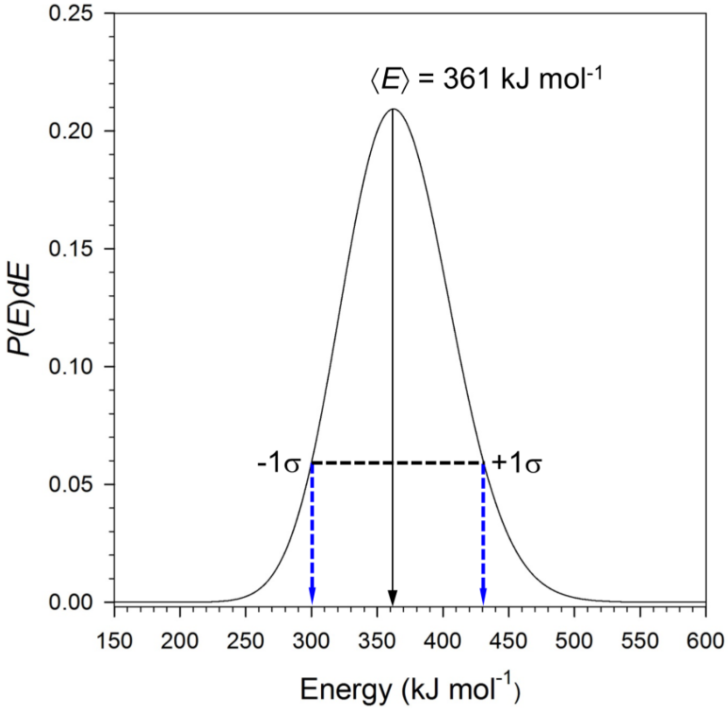

Figure S11. Calculated distribution of vibrational energies in complex **1** at 310 K. The broken-line arrows limit the area under one standard deviation from the 361 kJ mol^{-1} mean energy.

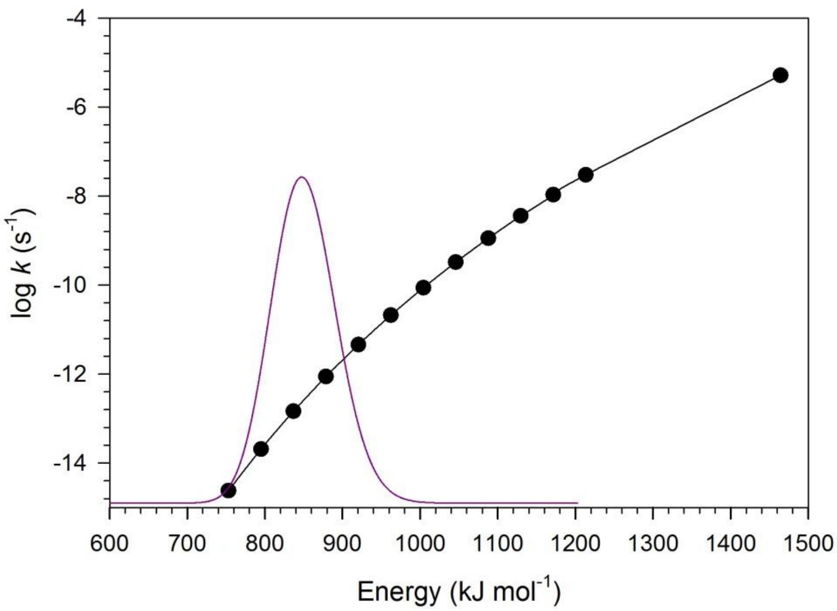

Figure S12. RRKM rate constants (log *k*, s^{-1}) for dissociation of complex (**1**-N_2) to monomer **10** and **11**. The pink curve shows the distribution, *P*(*E*)*dE*, 0.00-0.21, of internal energies in (**1**-N_2) formed by photodissociation and carbene to olefin isomerization.