Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

4-Hydrazinoquinazoline acting as reactive matrix for rapid and sensitive analysis of neutral and sialylated glycans using MALDI MS

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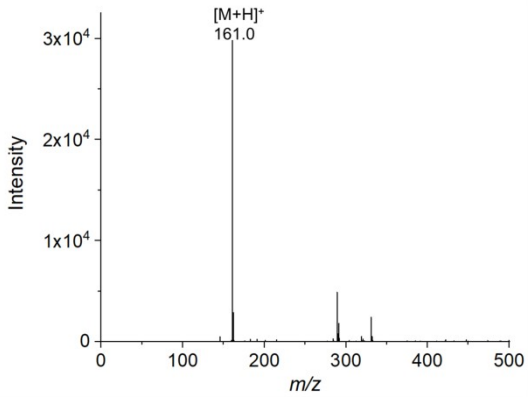


Fig. S1. MALDI mass spectrum of 4-HQ.

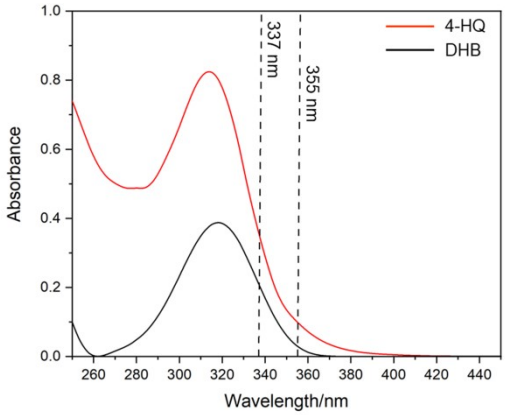


Fig. S2. UV−vis absorption spectra of 4-HQ and DHB (each at concentrations of 10^{-4} M in water).

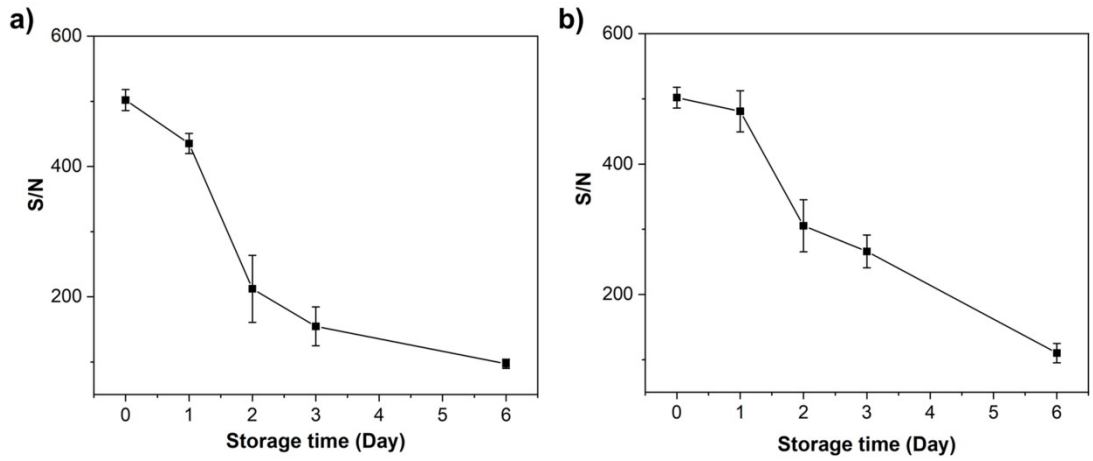


Fig. S3. S/N ratio variations of DP7 (5 pmol) with increasing storage time: a) 4-HQ matrix solution was stored at 4°C; b) sample was placed on MALDI target at room temperature.

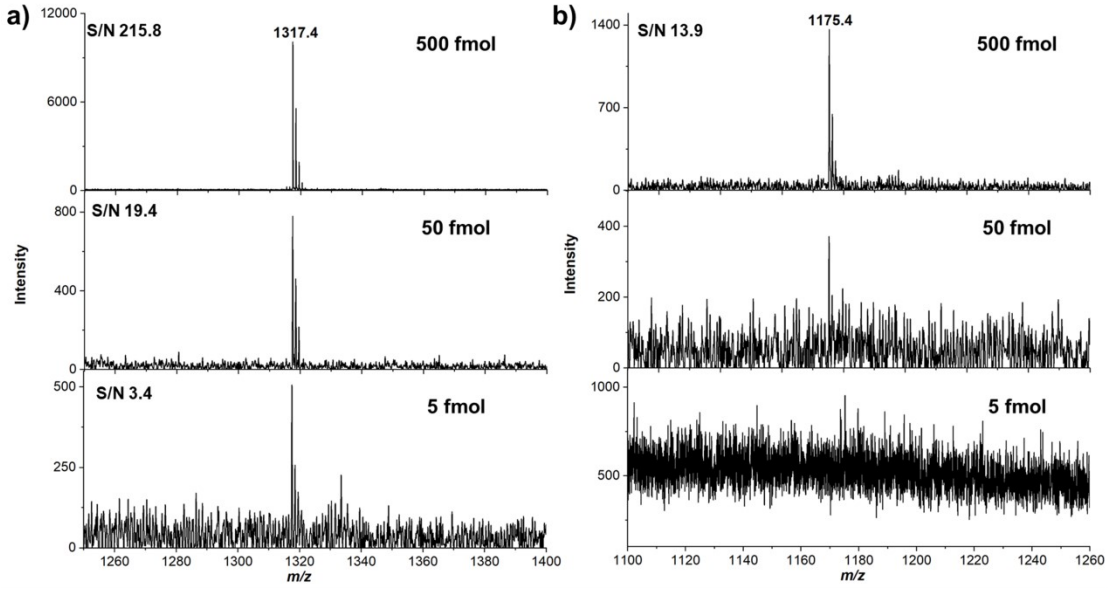


Fig. S4. MALDI mass spectra of different amount of DP7 using **a)** 4-HQ as a reactive matrix and **b)** DHB as the matrix.

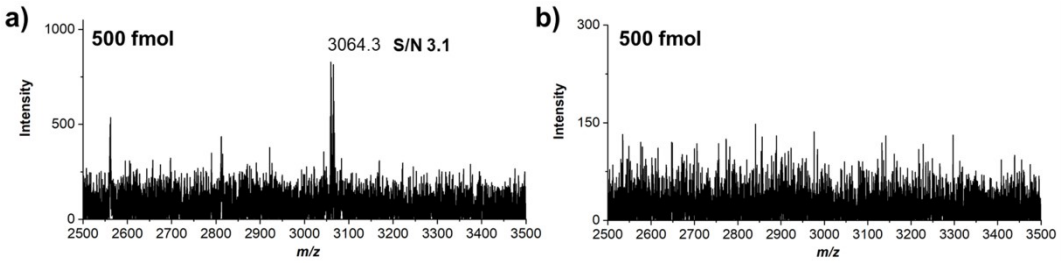


Fig. S5. MALDI mass spectra of A3 glycan using **a)** 4-HQ as a reactive matrix and **b)** DHB as the matrix.

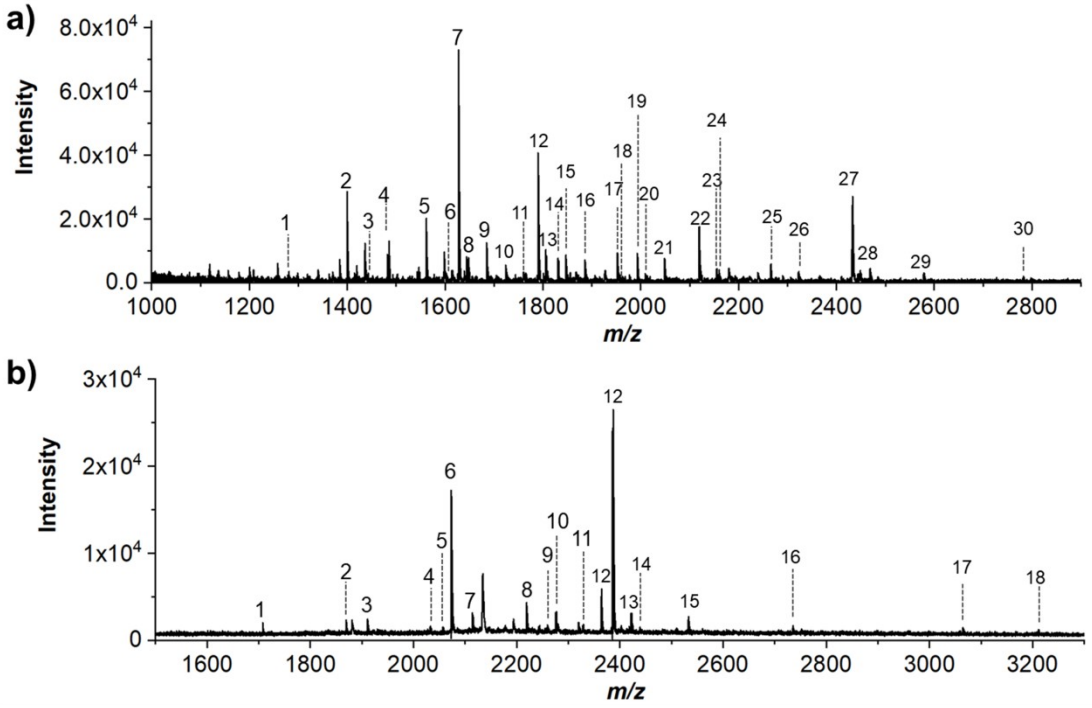
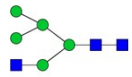
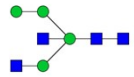
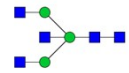
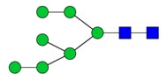
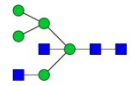
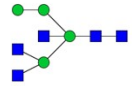
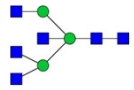
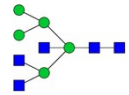
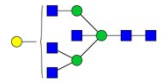
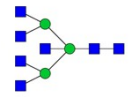
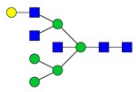
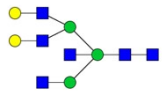
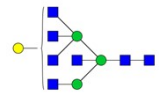
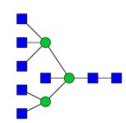
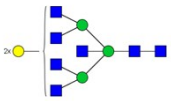
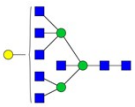
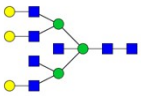
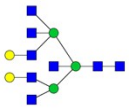


Fig. S6. MALDI mass spectra of N-glycans released from human serum using 4-HQ as a reactive matrix in **a)** positive and **b)** negative ion mode.

Table S1. List of identified N-glycans released from ovalbumin using 4-HQ or DHB as matrix. The m/z values are corresponding to the ions of $[M+Na]^+$.

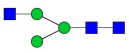
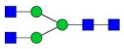
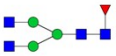
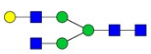
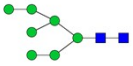
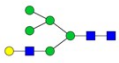
Peak No.[a]	Theoretical m/z of native glycans	Observed m/z of native glycans	Theoretical m/z of 4-HQ-labeled glycans	Observed m/z of 4-HQ-labeled glycans	Composition
1	933.3	933.3	1075.4	1075.4	
2	1095.4	–	1237.4	1237.4	
3	1136.4	1136.4	1278.5	1278.4	
4	1257.4	1257.4	1399.5	1399.5	
5	1298.4	1298.4	1440.5	1440.5	
6	1339.5	1339.5	1481.5	1481.5	
7	1419.5	1419.5	1561.5	1561.5	

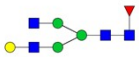
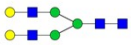
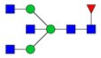
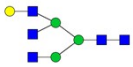
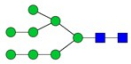
8	1460.5	–	1602.5	1602.5	
9	1501.5	1501.5	1643.6	1643.6	
10	1542.6	1542.6	1684.6	1684.6	
11	1581.5	–	1723.6	1723.6	
12	1663.6	1663.6	1805.6	1805.6	
13	1704.6	1704.6	1846.7	1846.7	
14	1745.6	1745.6	1887.7	1887.7	
15	1866.7	–	2008.7	2008.7	
16	1907.7	1907.7	2049.7	2049.7	
17	1948.7	1948.7	2090.8	2090.7	
18	2028.7	–	2170.8	2170.7	
19	2069.7	–	2211.8	2211.8	
20	2110.8	2110.7	2252.8	2252.8	
21	2151.8	2151.7	2293.8	2293.8	

22	2272.8	–	2414.9	2414.9	
23	2313.8	2313.8	2455.9	2455.9	
24	2434.9	–	2576.9	2576.9	
25	2475.9	2475.8	2617.9	2617.9	

[a]The numbers are corresponding to the peak numbers labeled in Fig. 5a, b.

Table S2. List of identified N-linked glycans released from human serum using 4-HQ as a reactive matrix in the positive ion mode. The m/z values are corresponding to the ions of $[M+(n+1)Na-nH]^+$ (n represents the amount of sialic acid residues in glycan).

Peak No.[a]	Theoretical m/z of native glycans	Theoretical m/z of 4-HQ-labeled glycans	Observed m/z of 4-HQ-labeled glycans	Structure
1	1136.4	1278.4	1278.4	
2	1257.4	1399.5	1399.5	
3	1298.4	1440.5	1440.5	
4	1339.5	1481.5	1481.5	
5	1419.5	1561.5	1561.5	
6	1460.5	1602.6	1602.6	
7	1485.5	1627.6	1627.6	
8	1501.5	1643.6	1643.6	
9	1542.6	1684.6	1684.6	
10	1581.5	1723.6	1723.6	
11	1622.6	1764.6	1764.6	

12	1647.6	1789.6	1789.6	
13	1663.6	1805.6	1805.6	
14	1688.6	1830.7	1830.7	
15	1704.6	1846.7	1846.7	
16	1743.6	1885.6	1885.6	
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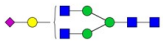
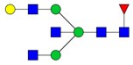
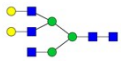
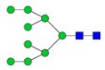
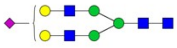
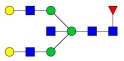
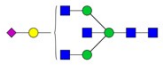
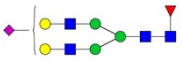
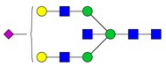
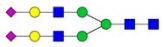
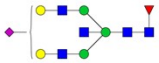
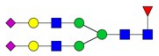
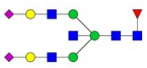
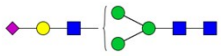
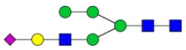
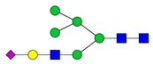
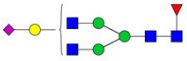
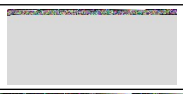
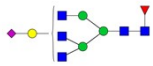
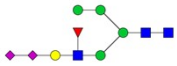
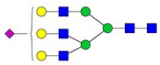
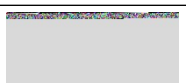
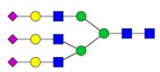
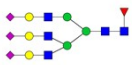
18	1814.6	1956.7	1956.7	
19	1850.7	1992.7	1992.7	
20	1866.7	2008.7	2008.7	
21	1905.6	2047.7	2047.7	
22	1976.7	2118.7	2118.7	
23	2012.7	2154.8	2154.8	
24	2017.7	2159.8	2159.8	
25	2122.7	2264.8	2264.8	
26	2179.8	2321.8	2321.8	
27	2289.8	2431.8	2431.8	
28	2325.8	2467.9	2467.9	
29	2435.8	2577.9	2577.9	
30	2638.9	2780.9	2780.9	

[a]The numbers are corresponding to the peak numbers labeled in Fig. S3a.

Table S3. List of identified N-linked glycans released from human serum using 4-HQ as a reactive matrix in the negative ion mode. The m/z values are corresponding to the ions of

$[M+(n-1)Na-nH]^-$ (n represents the amount of sialic acid residues in glycan).

Peak No.[a]	Theoretical m/z of native glycans	Theoretical m/z of 4-HQ-labeled glycans	Observed m/z of 4-HQ-labeled glycans	Structure
1	1565.6	1707.6	1707.6	
2	1727.6	1869.7	1869.7	
3	1768.6	1910.7	1910.7	
4	1889.7	2031.7	2031.7	
5	1914.7	2056.8	2056.8	
6	1930.7	2072.8	2072.8	
7	1971.7	2113.8	2113.8	
8	2076.7	2218.8	2218.8	
9	2117.8	2259.8	2259.8	
10	2133.8	2275.8	2275.8	
11	2186.8	2328.8	2328.8	
12	2243.8	2363.8 2385.8	2363.8 2385.8	
13	2279.8	2421.9	2421.9	
14	2295.8	2437.9	2437.9	
15	2389.8	2531.9	2531.9	
16	2592.9	2735.0	2735.0	
17	2922.0	3064.0	3064.0	
18	3068.1	3210.1	3210.1	

[a]The numbers are corresponding to the peak numbers labeled in Fig. S3b.