Supporting information

Design of hydrophilic mercaptosuccinic acid functionalized *β*-cyclodextrin polymer *via* host-guest interaction: toward highly efficient glycopeptide enrichment

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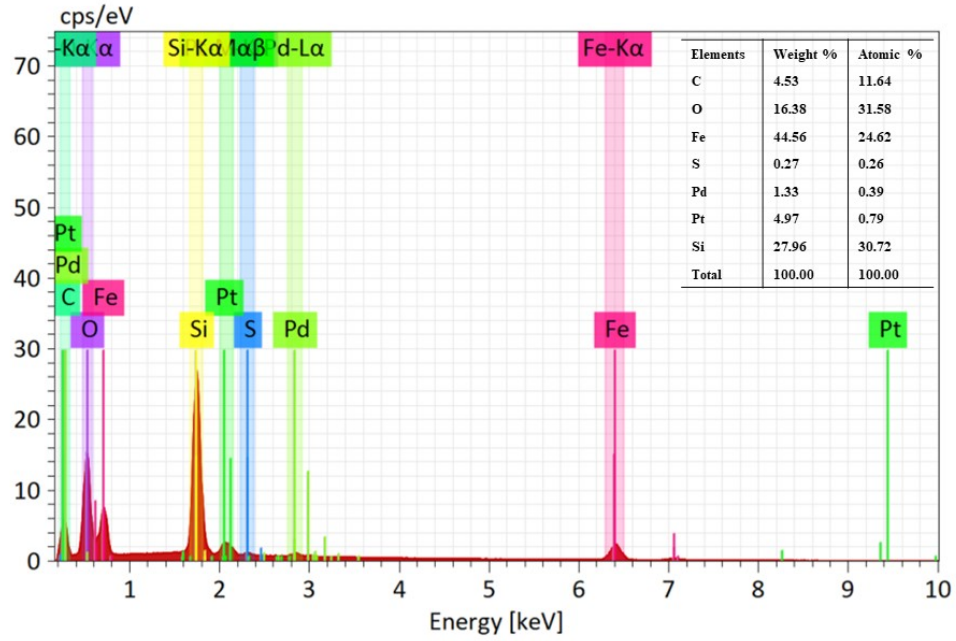

Fig. S1 EDS data of magCDP@Ada-MSA.

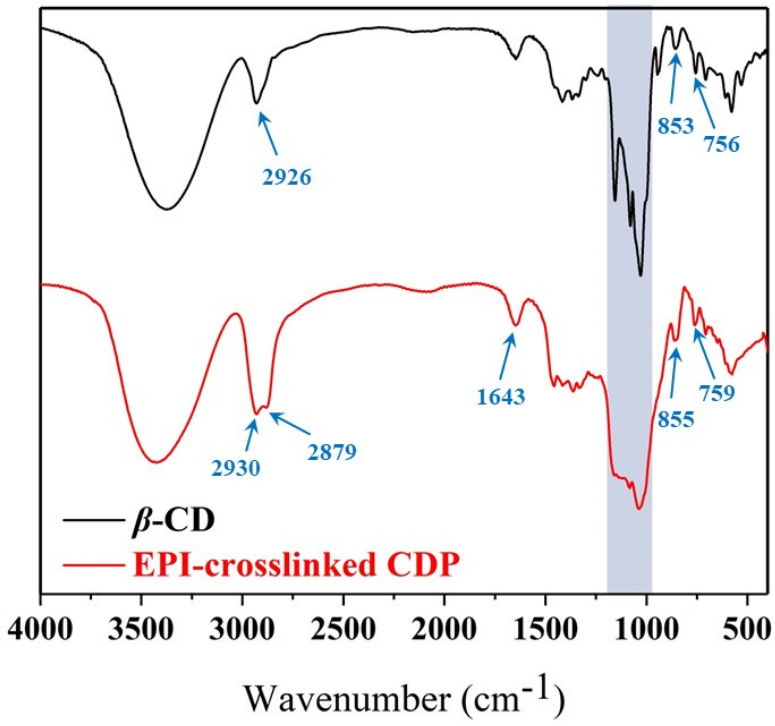

Fig. S2 FT-IR spectra of *β*-CD and EPI-crosslinked CDP.

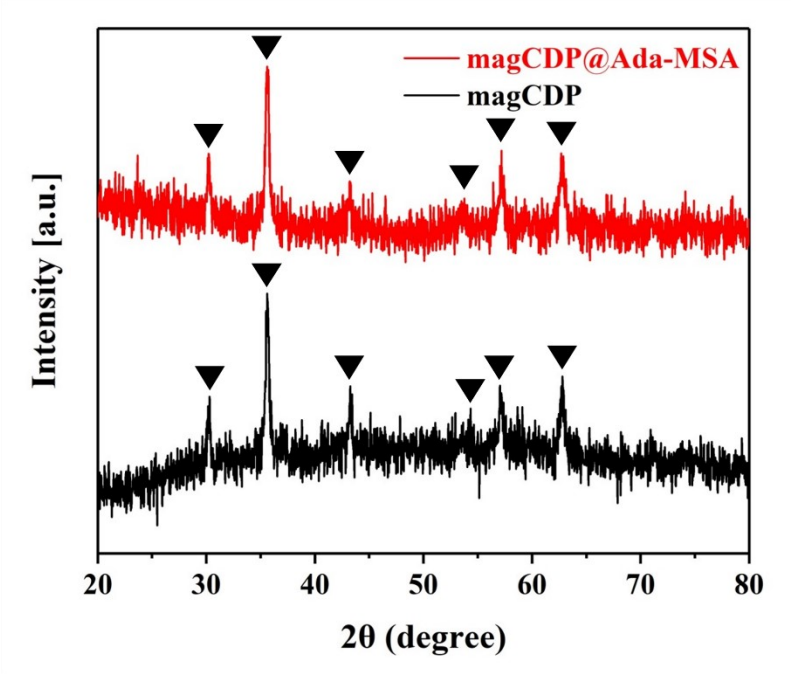

Fig. S3 XRD patterns of magCDP and magCDP@Ada-MSA. "▼" indicates the characteristic peaks of Fe_3O_4.

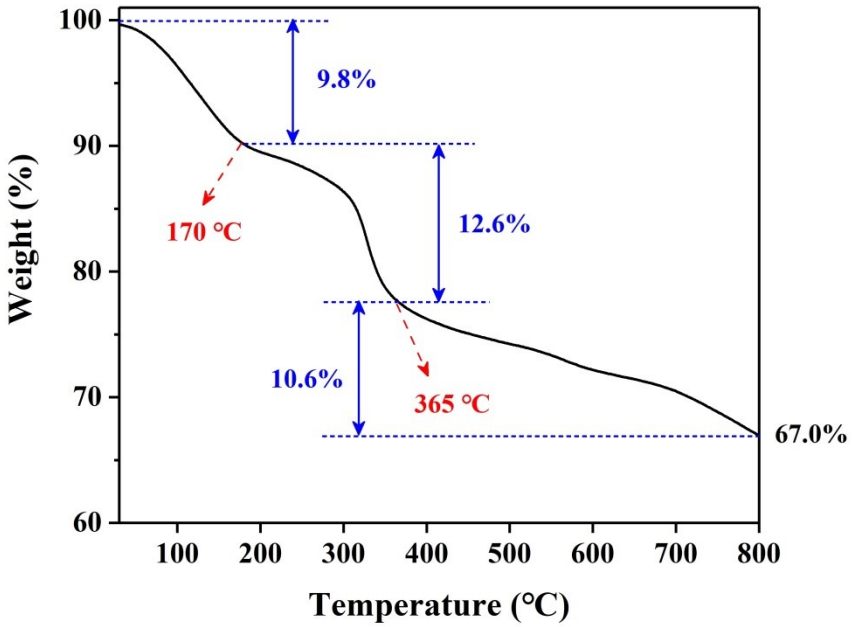

Fig. S4 TGA curve of magCDP@Ada-MSA.

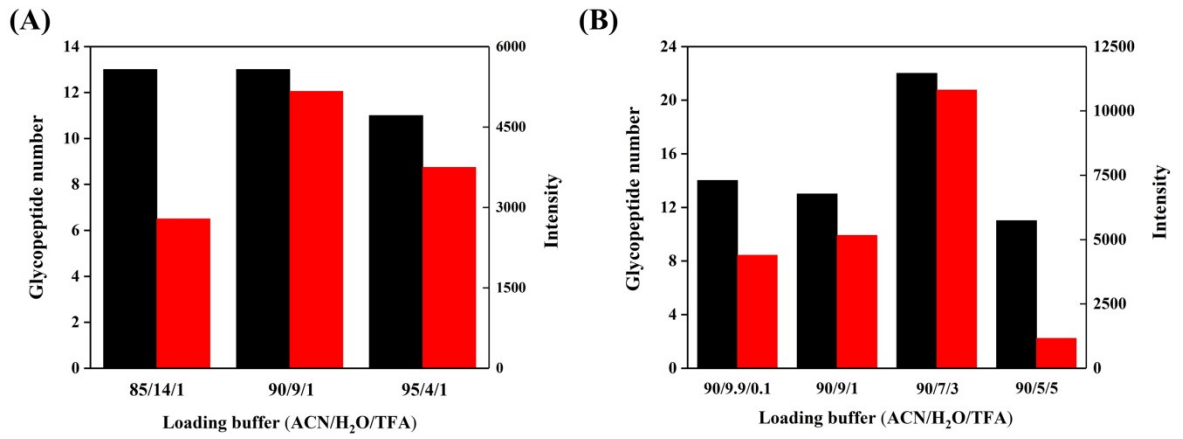

Fig. S5 Effect of loading buffers containing different concentrations of (A) ACN and (B) TFA on glycopeptides enriched by magCDP@Ada-MSA.

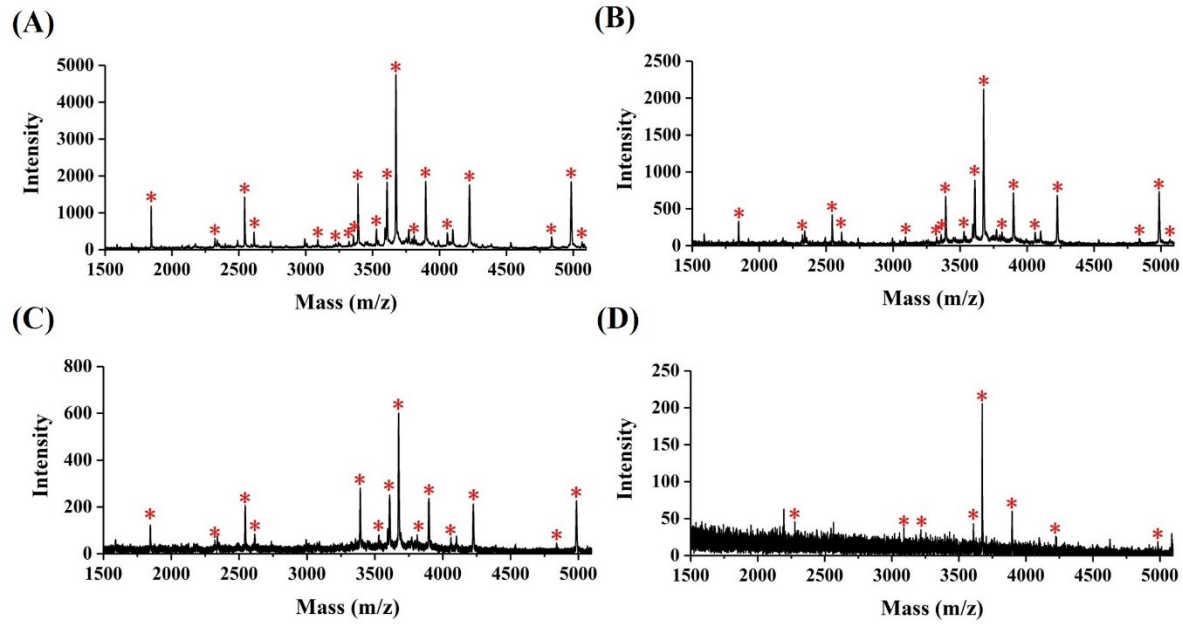

Fig. S6 MALDI-TOF mass spectra of standard HRP tryptic digests with the concentration of (A) 100, (B) 10, (C) 1, and (D) 0.1 fmol μL^{-1} treated by magCDP@Ada-MSA. "*" indicates glycopeptide.

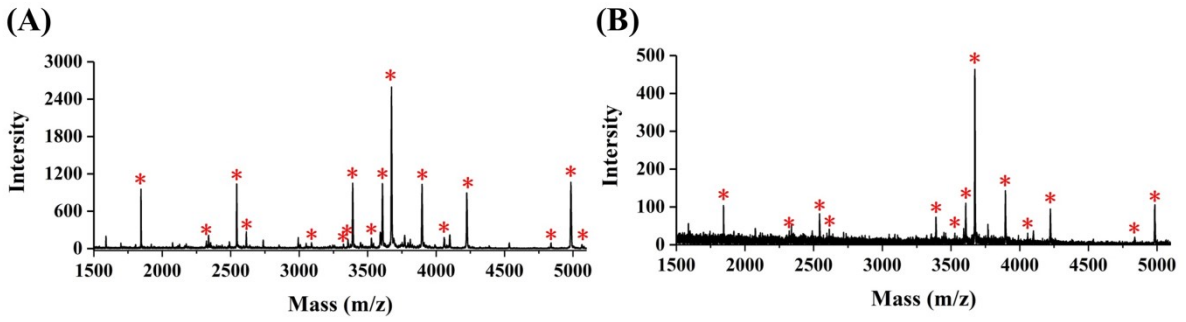

Fig. S7 MALDI-TOF mass spectra of HRP tryptic digests after enrichment by magCDP (A) 100 and (b) 10 fmol μL^{-1}. "*" indicates glycopeptide.

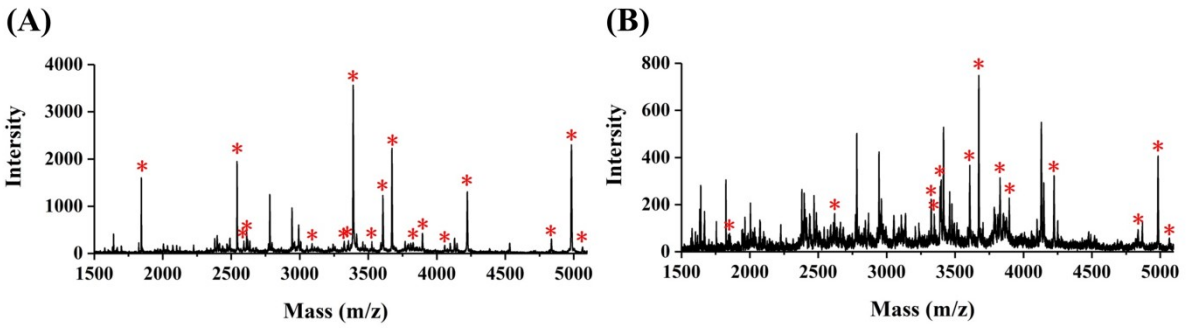

Fig. S8 MALDI-TOF mass spectra of mixtures of HRP and BSA tryptic digests after enrichment by magCDP (a) 1:10 and (b) 1:50. "*" indicates glycopeptide.

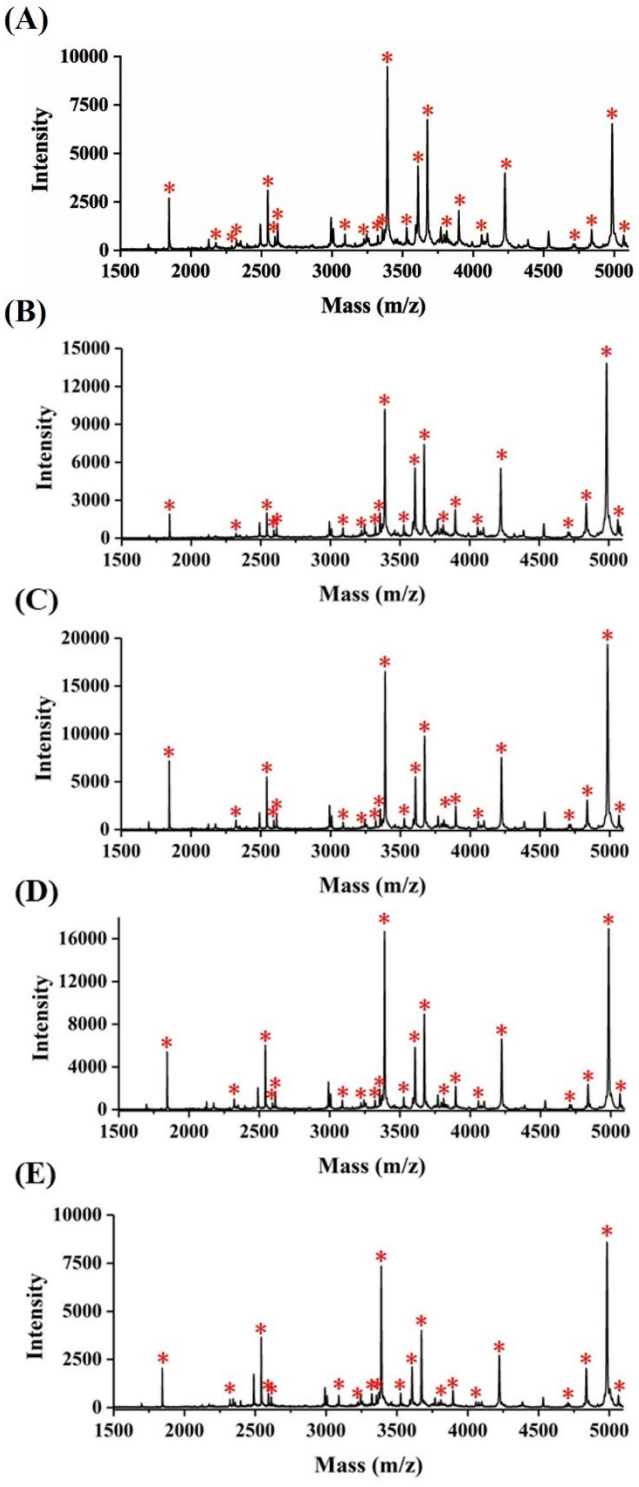

Fig. S9 MALDI-TOF mass spectra of HRP tryptic digests after enrichment by magCDP@Ada-MSA: (A) for the first time, (B) for the third time, (C) for the fifth time, (D) for the seventh time, and (E) for the tenth time. "*****" indicates glycopeptide.

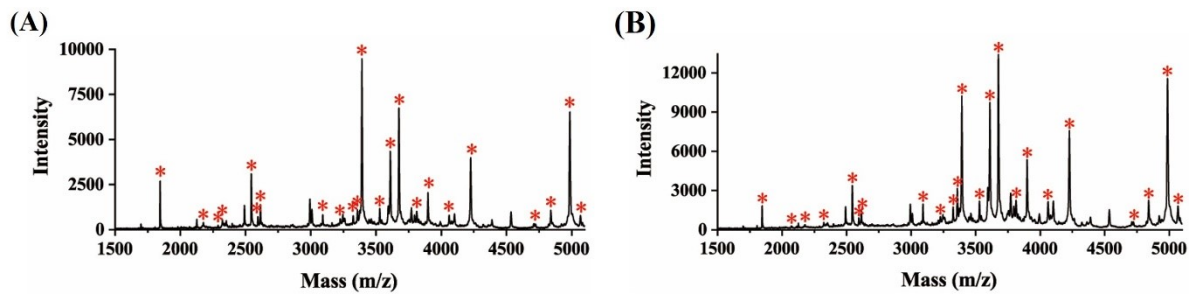

Fig. S10 MALDI-TOF mass spectra of HRP tryptic digests after enrichment by magCDP@Ada-MSA: (a) before and (b) after storage for 3 months.

Table S1 Detailed information about identified glycopeptides enriched from HRP digests by magCDP@Ada-MSA. N#: N-glycosylation site.

magCDP@Ada-MSA			
Peak	Observed (m/z)	Glycan composition	Amino acid sequence
H1	1842.1	XylMan3FucGlcNAc2	NVGLN#R
H2	2175.4	Man3GlcNAc2Fuc	LYN#FSN#TGLP
H3	2290.6	XylMan2GlcNAc2	SILLDN#TTSFR
H4	2318.7	Man3GlcNAc2	PTLN#TTYLQTLR
H5	2543.2	FucGlcNAc	SFAN#STQTFFNAFVEAMDR
H6	2590.1	XylMan3FucGlcNAc2	PTLN#TTYLQTLR
H7	2612.1	XylMan3GlcNAc2	MGN#ITPLTGTQGQIR
H8	3088.5	XylMan3FucGlcNAc2	GLCPLNGN#LSALVDFDLR
H9	3221.5	XylMan3FucGlcNAc2	LHFHDCFVNGCDASILLDN#TTSFR
H10	3321.9	XylMan3FucGlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H11	3354.5	XylMan3FucGlcNAc2 XylMan 3GlcNAc 2	LYN#FSNTGLPDPTLN#TTYLQTLR
H12	3388.8	XylHex6HexNAc4Fuc2	DSFRNVGLN#R
H13	3525.4	XylMan3GlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
H14	3607.8	XylMan3GlcNAc2Fuc	NQCRGLCPLNGN#LSALVDFDLR
H15	3671.9	XylMan3GlcNAc2Fuc	GLIQSDQELFSSPN#ATDTIPLVR
H16	3812.2	XylMan3FucGlcNAc2	LHFHDCFVNGCDASILLDN#TTSFR
H17	3895.1	XylMan3GlcNAc2Fuc	LHFHDCFVNGCDASILLDN#TTSFR
H18	4057.2	XylMan4GlcNAc2Fuc	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H19	4221.8	XylMan3GlcNAc2Fuc	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H20	4720.9	Man3FucGlcNAc2 Man3FucGlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
H21	4838.5	XylMan3FucGlcNAc2 XylMan3GlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
H22	4984.7	XylMan3GlcNAc2Fuc	LYN#FSNTGLPDPTLN#TTYLQTLR
H23	5066.0	Xyl Man3GlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
magCDP			
Peak	Observed (m/z)	Glycan composition	Amino acid sequence
H1	1842.8	XylMan3FucGlcNAc2	NVGLN#R
H2	2321.9	Man3GlcNAc2	PTLN#TTYLQTLR
H3	2542.3	FucGlcNAc	SFAN#STQTFFNAFVEAMDR
H4	2592.4	XylMan3FucGlcNAc2	PTLN#TTYLQTLR
H5	2612.7	XylMan3GlcNAc2	MGN#ITPLTGTQGQIR
H6	3088.9	XylMan3FucGlcNAc2	GLCPLNGN#LSALVDFDLR
H7	3323.6	XylMan3FucGlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H8	3355.3	XylMan3FucGlcNAc2 XylMan 3GlcNAc 2	LYN#FSNTGLPDPTLN#TTYLQTLR

H9	3388.0	XylHex6HexNAc4Fuc2	DSFRNVGLN#R
H10	3526.5	XylMan3GlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
H11	3606.9	XylMan3GlcNAc2Fuc	NQCRGLCPLNGN#LSALVDFDLR
H12	3673.1	XylMan3GlcNAc2Fuc	GLIQSDQELFSSPN#ATDTIPLVR
H13	3896.1	XylMan3GlcNAc2Fuc	LHFHDCFVNGCDASILLDN#TTSFR
H14	4057.3	XylMan4GlcNAc2Fuc	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H15	4223.1	XylMan3GlcNAc2Fuc	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
H16	4837.8	XylMan3FucGlcNAc2 XylMan3GlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
H17	4983.2	XylMan3GlcNAc2Fuc	LYN#FSNTGLPDPTLN#TTYLQTLR
H18	5065.9	Xyl Man3GlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR

Table S2 Detailed information about identified glycopeptides enriched from human serum by magCDP@Ada-MSA. N#: N-glycosylation site.

Peak	Observed (m/z)	Amino acid sequence
1	1528.3	cIQAN#YSLMENGK
2	1535.8	LLDLSGNN#LTHLPK
3	1640.9	TKPREEQFN#STFR
4	1678.1	VTAcHSSQPN#ATLYK
5	1719.0	QVHFFVN#ASDVDNVK
6	1778.4	SLPNFPN#TSATAN#ATGGR
7	1820.8	VFHIHN#ESWVLLTPK
8	1883.9	LHINHNN#LTESVGPLPK
9	1894.1	EHEGAIYPDN#TTDFQR
10	1920.4	SVVAPATDGGLN#LTSTFLR
11	1974.9	cATPHGDN#ASLEATFVKR
12	1987.6	LQAILGVPWKDKN#cTSR
13	1999.0	N#EcFLQHKDDN#PNLPR
14	2023.5	ELHHLQEQN#VSNAFLDK
15	2046.0	LSDLSIN#STEcLHVHcR
16	2149.2	IIVPLNNREN#ISDPTSPLR
17	2165.4	VSN#QTLSLFFTVLQDVPVR
18	2233.1	LDAPTNLQFVN#ETDSTVLVR
19	2278. 8	IYSN#HSALESLALIPLQAPLK
20	2401.4	FN#LTETSEAEIHQSFQHLLR
21	2414.9	AAPAPQEATATFN#STADREDGHR
22	2449.8	GLQPTLTNPGEcRPN#FTcAcR
23	2458.1	ALGISPFHEHAEVVFTAN#DSGPR
24	2488.9	KEHETcLAPELYN#GN#YSTTQK
25	2562.8	KcPLPEN#ITHILVHGDDFSVNR
26	2606.1	ALGISPFHEHAEVVFTAN#DSGPRR
27	2622.1	HGIQYFNN#NTQHSSLFMLNEVK
28	2635.8	QLVEIEKVVLHPN#YSQVDIGLIK
29	2763.9	EEQFN#STFR
30	2780.8	ITYSIVQTN#cSKEN#FLFLTPDcK
31	2796.0	HGIQYFnN#NTQHSSLFmLNEVKR
32	2841.9	FVEGSHN#STVSLTTK
33	2903.8	ELHHLQEQN#VSNAFLDKGEFYIGSK
34	2929.8	IcDLLVANNHFAHFFAPQN#LTNMNK
35	2958.0	SRYPHKPEIN#STTHPGADLQEN#FcR

36	2980.9	EEQYN#STYRVVSVLTVLHQDWLN#GK
37	3007.9	SIPAcVPWSPYLFQPN#DTcIVSGWGR
38	3051.7	N#LSSLESVQLDHN#QLETLPGDVFGALPR
39	3165.1	GYTLAGDKESScLAN#SSWSHSPPVcEPVK
40	3183.5	QLAHQSN#STnIFFSPVSIATAFAMLSLGTK
41	3205.2	GGnSnGALcHFPFLYNNHN#YTDcTSEGR
42	3220.0	LSHNELADSGIPGNSFN#VSSLVELDLSYNK
43	3355.3	DTAVFEcLPQHAMFGN#DTITcTTHGN#WTK
44	3373.9	FSLLGHASIScTVEN#ETIGVWRPSPPTcEK
45	3399.8	EEQYN#STYRVVSVLTVLHQDWLN#GKEYK
46	3455.8	NSVLN#SSTAEHSSPYSEDPIEDPLQPDVTGIR
47	3531.6	ncGVN#cSGDVFTALIGEIASPN#YPKPYPEN#SR
48	3552.1	QVFPGLN#YcTSGAYSN#ASSTDSASYYPLTGDTR

Table S3 Detailed information about identified glycopeptides enriched from human saliva by magCDP@Ada-MSA. N#: N-glycosylation site.

Peak	Observed (m/z)	Amino acid sequence
1	827.7	AIN#DTAAR
2	953.6	TPLTAN#ITK
3	970.9	INGN#cTGIK
4	1155.1	EEQFN#STFR
5	1170.3	EEQFN#STYR
6	1189.8	EEQYN#STYR
7	1227.1	EN#ISDPTSPLR
8	1282.0	YKN#NSDISSTR
9	1398.1	VPGN#VTAVLGETLK
10	1407.9	GLN#LTEDTYKPR
11	1463.5	NLFLN#HSEN#ATAK
12	1524.6	LVNLN#SSYGLcAGR
13	1537. 2	ADEGSLKN#ISIYTK
14	1548.0	YDFN#SSmLYSTAK
15	1564.5	ISEEN#ETTcYMGK
16	1604.5	FVEGSHN#STVSLTTK
17	1666.2	HYTN#SSQDVTVPcR
18	1680.1	N#GIYN#ITVLASDQGGR
19	1735.5	ALPQPQN#VTSLLGcTH
20	1772.0	VcQDcPLLAPLN#DTR
21	1795.3	VVLHPN#YSQVDIGLIK
22	1855.9	N#GTGHGN#STHHGPEYMR
23	1868.0	LGAcN#DTLQQLMEVFK
24	1892.3	EHEGAIYPDN#TTDFQR
25	1903.5	FGcEIEN#NRSSGAFWK
26	1924.4	QnQcFYN#SSYLNVQR
27	2068.0	DIVEYYN#DSN#GSHVLQGR
28	2078.1	AFGQFFSPGEVIYN#KTDR
29	2093.2	NPVGLIGAEN#ATGETDPSHSK
30	2167.0	VS N#QTLSLFFTVLQDVPVR
31	2192.9	LGSFEGLVN#LTFIHLQHNR
32	2207.3	DVQIIVFPEDGIHGFN#FTR
33	2248.5	LQAPLN#YTEFQKPIcLPSK
34	2256.5	ADGTVNQIEGEATPVN#LTEPAK
35	2317.0	LYLGSN#NLTALHPALFQN#LSK
36	2340.3	GLTFQQN#ASSMcVPDQDTAIR
37	2425.5	VPGN#VTAVLGETLKVPcHFPcK
38	2451.9	ALGISPFHEHAEVVFTAN#DSGPR
39	2611.2	LGHcPDPVLVNGEFSSSGPVN#VSDK
40	2739.1	LFGDKSLTFN#ETYQDISELVYGAK

Table S4. Comparison of the numbers of glycopeptides captured from complex biological samples by magCDP@Ada-MSA with other reports.

Materials	Sample	Detection Method	Number of glycopeptides	Ref.
FSAu@mSiO_2@L-Cys	Human saliva	LC-MS/MS	40	1
SiO_2@L-Cys capillary packed columns	Human saliva	LC-MS/MS	69	2
Fe_3O_4@mTiO_2-MSA	Human saliva	Nano-LC-MS/MS	65	3
Fe_3O_4@Au-GSH	Human serum	MALDI-TOF MS	22	4
Fe_3O_4@TA@Ag@L-Cys	Human serum	MALDI-TOF MS	56	5
magCDP@Ada-MSA	Human saliva	MALDI-TOF MS	37	This work
	Human serum		48	
	Human saliva		40	

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