

Supporting Information

A Novel Hydrophilic Hydrogel with 3D Network Structure for Highly Efficient Enrichment of N-glycopeptides

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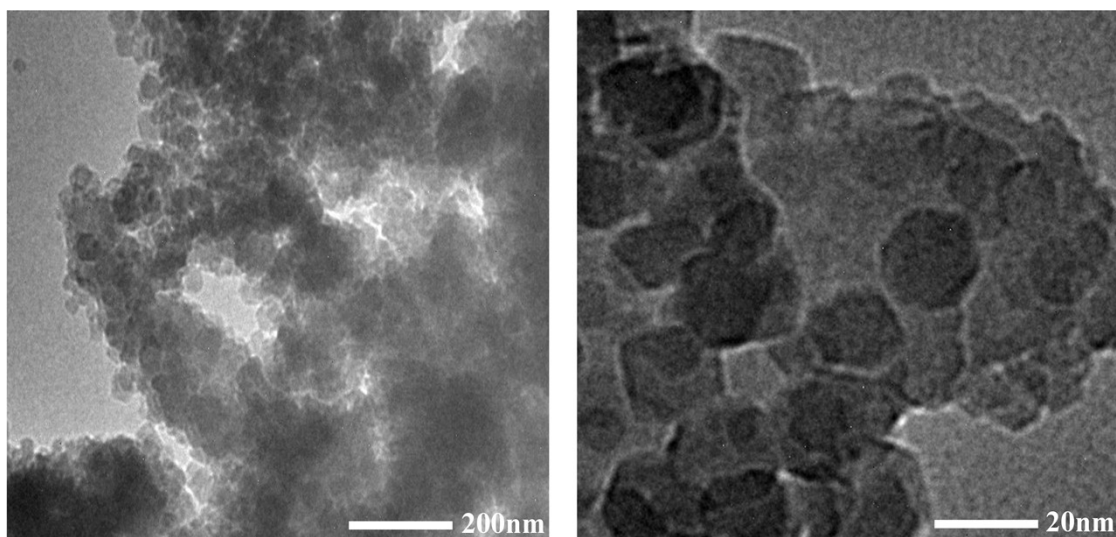


Figure S1. TEM image of the ZIF-8/SAP.

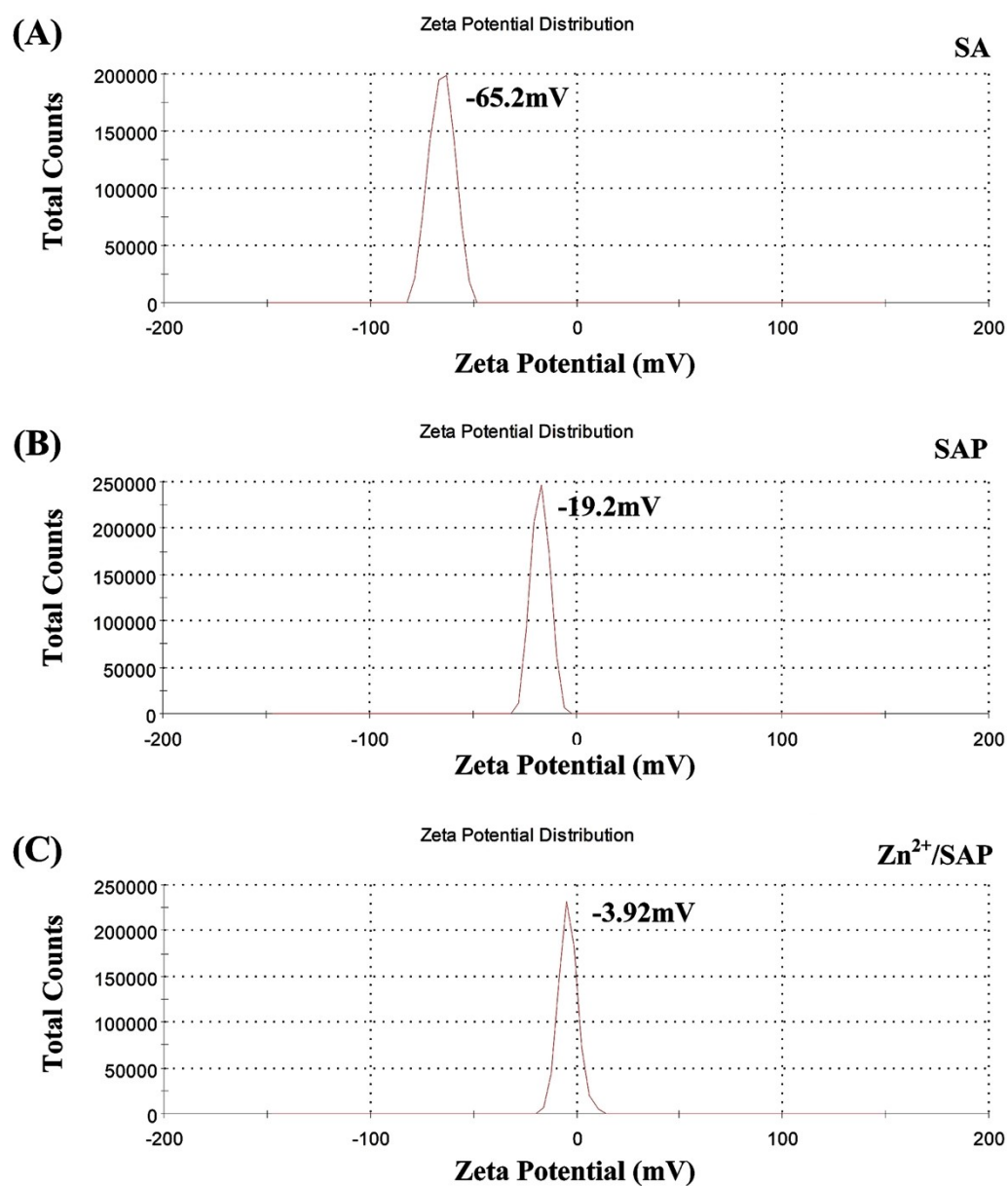


Figure S2. Zeta potential of SA, SAP and Zn²⁺/SAP.

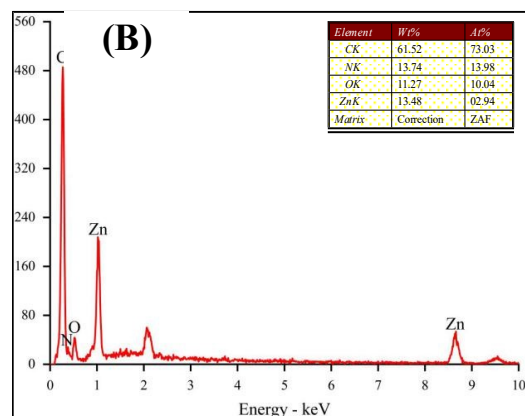
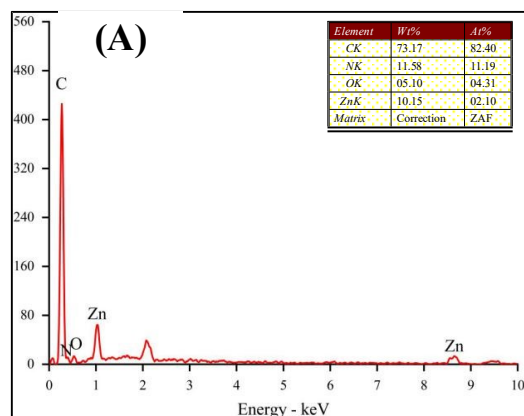


Figure S3. The EDS spectra data of (A) Zn^{2+} /SAP and (B) ZIF-8/SAP.

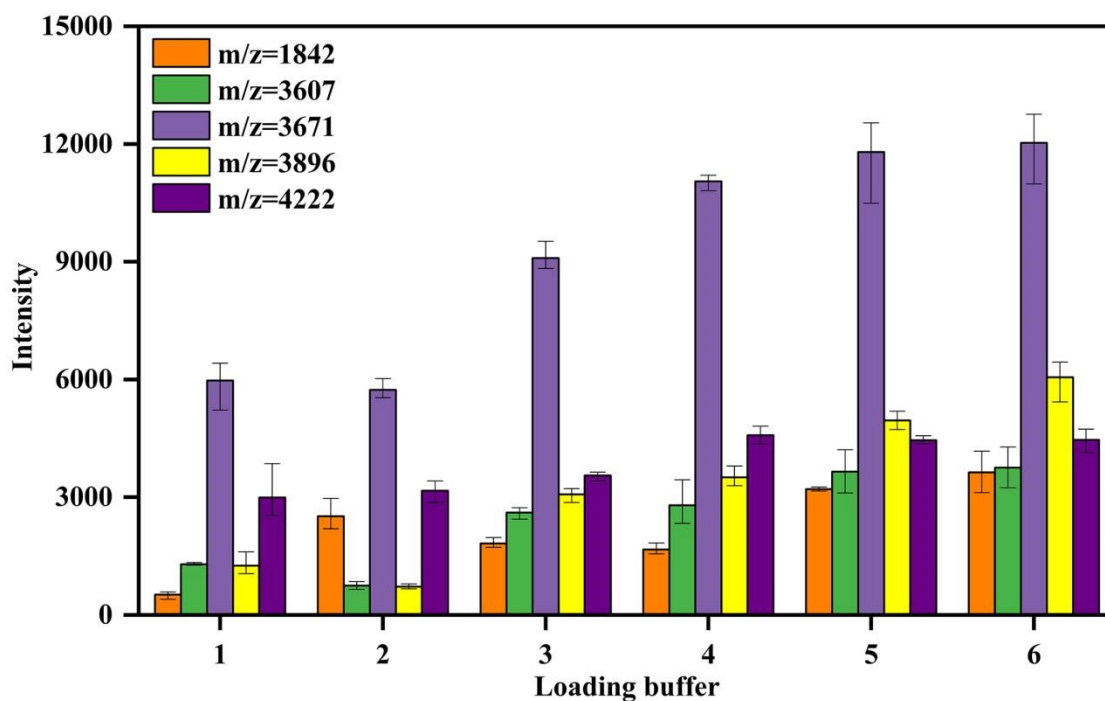


Figure S4. Optimization of the loading buffer for glycopeptide enrichment with ZIF-8/SAP. (1) ACN/ H_2O /TFA, 90/9.9/0.1, v/v/v; (2) ACN/ H_2O /TFA, 90/9/1, v/v/v; (3) ACN/ H_2O /TFA, 92/7.9/0.1, v/v/v; (4) ACN/ H_2O /TFA, 92/7/1, v/v/v; (5) ACN/ H_2O /TFA, 95/4.9/0.1, v/v/v; (6) ACN/ H_2O /TFA, 95/4/1, v/v/v.

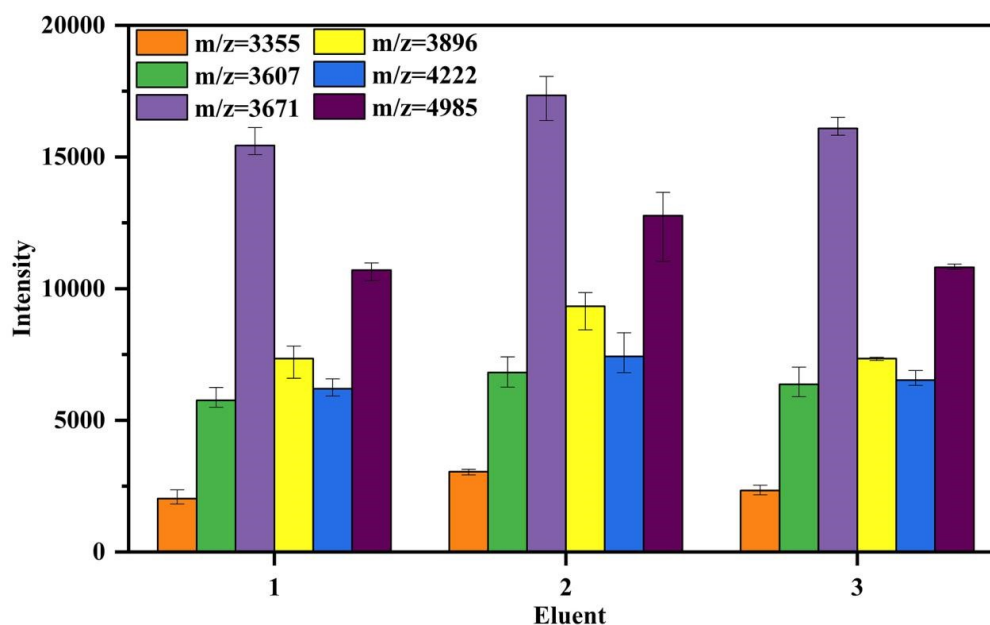


Figure S5. Optimization of the elute solution for glycopeptide enrichment with ZIF-8/SAP. (1) ACN/ H_2O /TFA, 30/69/1, v/v/v; (2) ACN/ H_2O /TFA, 35/64/1, v/v/v; (3) ACN/ H_2O /TFA, 40/59/0.1, v/v/v.

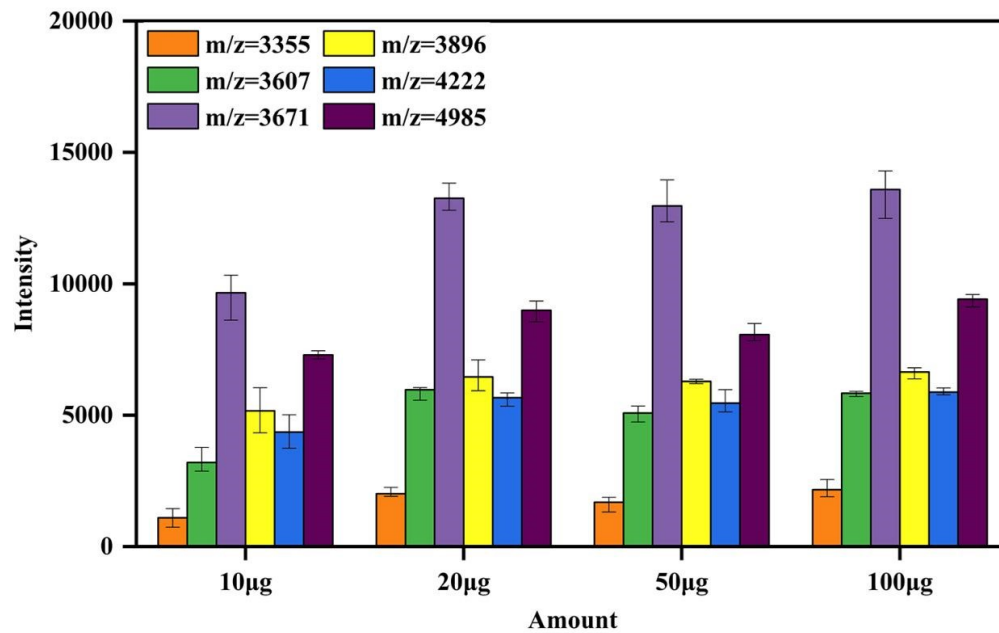


Figure S6. Enrichment binding capacity evaluation of ZIF-8/SAP for glycopeptides.

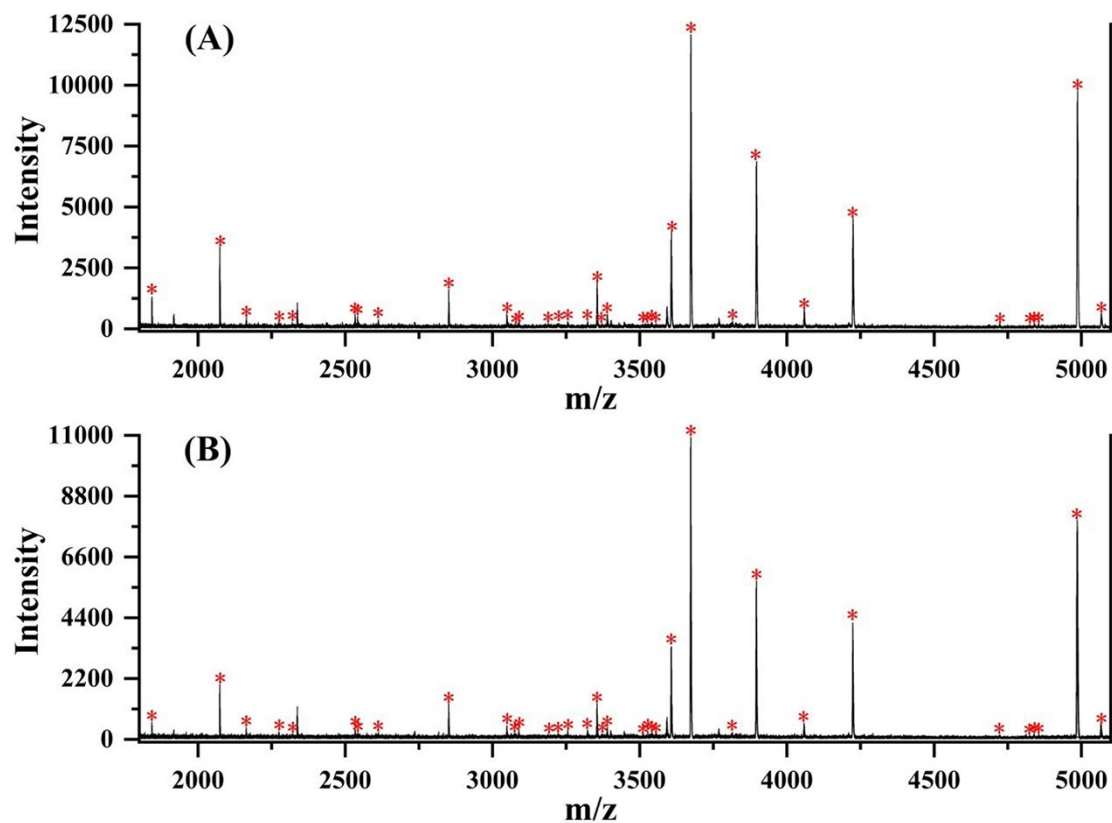


Figure S7. Reusability test of ZIF-8/SAP using tryptic digested HRP. After (A) first time and (B) seventh time.

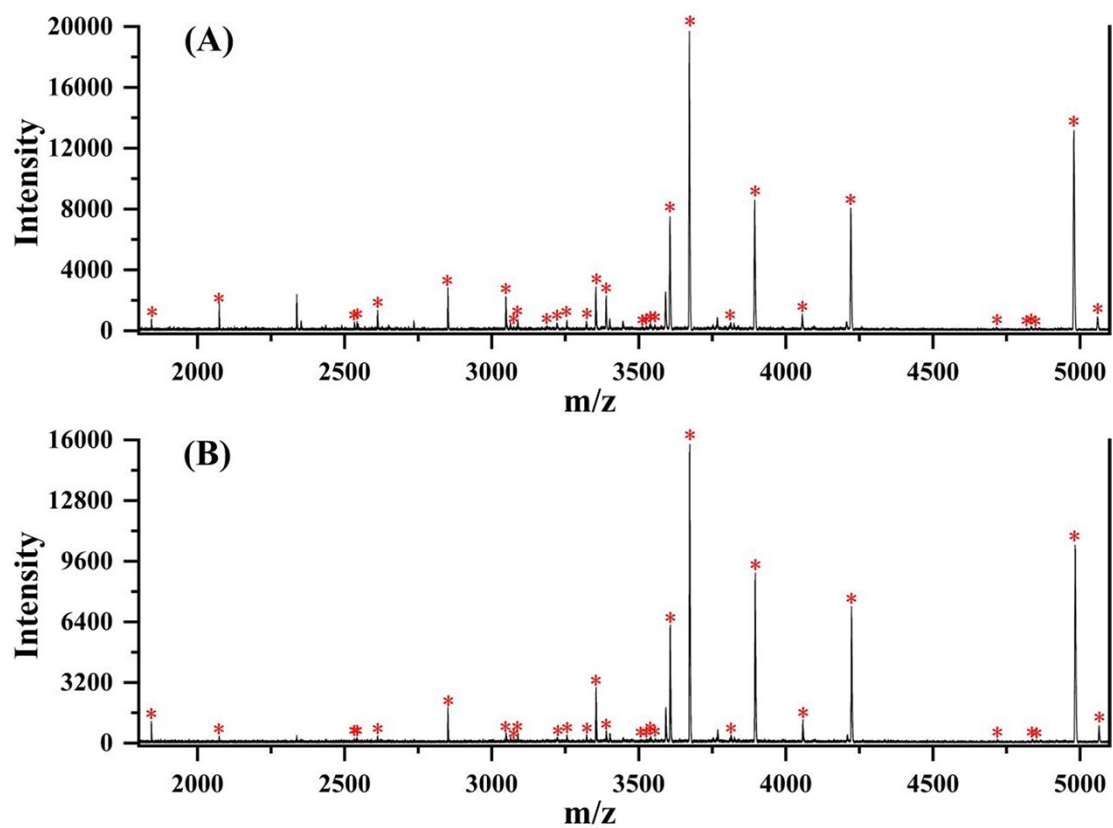


Figure S8. The stability of ZIF-8/SAP after being stored at room temperature for (A) the first week and (B) the tenth week.

Table S1. Detailed information of the observed glycopeptides obtained from HRP tryptic digests. The *N*-glycosylation sites are marked with N#. GlcNAc = *N*-acetylglucosamine, Fuc = fucose, Man = mannose, Xyl = xylose.

NO.	m/z	Glycan	Peptide sequence
1	1842	XylMan3FucGlcNAc2	NVGLN#R
2	2074	XylMan3GlcNAc2	PN#VSNIVR
3	2164	Man3GlcNAc2Xyl	LYN#FSN#TGLP
4	2274	Man3GlcNAc2	DSFRNVGLN#R
5	2320	Man2GlcNAc2	MGN#ITPLTGTQGQIR
6	2532	FucGlcNAc	SFAN#STQTFNFAVEAMDR
7	2542	XylMan3FucGlcNAc2	SSPN#ATDTIPLVR
8	2612	XylMan3GlcNAc2	MGN#ITPLTGTQGQIR
9	2851	FucGlcNAc	GLIQSDQELFSSPN#ATDTIPLVR
10	3048	XylMan2GlcNAc2	SFAN#STQTFNFAVEAMDR
11	3075	FucGlcNAc2	LHFHDCFVNGCDASILLDN#TTSFR
12	3087	XylMan3FucGlcNAc2	GLCPLNGN#LSALVDFDLR
13	3189	XylMan2FucGlcNAc2	SFAN#STQTFNFAVEAMDR
14	3223	Man3FucGlcNAc2	SFAN#STQTFNFAVEAMDR
15	3257	XylMan3FucGlcNAc2	SFAN#STQTFNFAVEAMDR
16	3322	XylMan3FucGlcNAc2	QLTPTFYDNSCPN#VSNIVR
17	3355	XylMan3FucGlcNAc2	SFAN#STQTFNFAVEAMDR
18	3371	XylHex3FucHexNAc2	SFAN#STQTFNFAVEAMDR
19	3388	XylMan3FucGlcNAc2	DSFRNVGLN#R
20	3508	XylMan2FucGlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
21	3527	XylMan3GlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
22	3539	Man3FucGlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
23	3555	XylMan3FucGlcNAc2	SFAN#STQTFNFAVEAMDR
24	3607	XylMan3FucGlcNAc2	NQCRGLCPLNGN#LSALVDFDLR
25	3671	XylMan3FucGlcNAc2	GLIQSDQELFSSPN#ATDTIPLVR
26	3813	Man2GlcNAc2	LHFHDCFVNGCDASILLDN#TTSFRTEK
27	3896	XylMan3FucGlcNAc2	LHFHDCFVNGCDASILLDN#TTSFR
28	4056	XylMan3GlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
29	4222	XylMan3FucGlcNAc	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR
30	4720	Man3FucGlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
31	4821	XylMan2FucGlcNAc2, XylMan2GlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
32	4839	XylMan3FucGlcNAc2, XylMan3GlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
33	4853.5	XylMan3 FucGlcNAc2, XylMan3GlcNAc2	LYN#FSNTGLPDPTLN#TTYLQTLR
34	4985	XylMan3FucGlcNAc2,	LYN#FSNTGLPDPTLN#TTYLQTLR

		XylMan3FucGlcNAc2	
35	5067	XylMan3GlcNAc2	QLTPTFYDNSC(AAVESACPR)PN#VSNIVR

Table S2. Detailed information of the glycopeptides enriched by ZIF-8/SAP from 10 μ L of human serum tryptic digests. n denotes the identified N-linked glycosylation site.

NO.	Protein	Peptide Sequence	m/z [Da]
1	P26927	GTAnTTTAGVPCQR	717.83516
2	P08519	WEYCnLTR	571.74974
3	P00742	GDNnLTR	395.68809
4	Q06033	EnLTAR	352.68248
5	P09871	NCGVnCSGDVFTALIGEIASPNYPKPYPENSR	1176.54805
6	P05546	DFVnASSK	434.70598
7	P41222	WFSAGLASnSSWLR	791.89195
8	P29622	FLnDTMAVYEAK	709.82823
9	P00751	FLCTGGVSPYADPnTCR	958.42791
10	P02675	nYCGLPGEYWLGN DK	893.89188
11	P07358	LLCNGDnDCGDQSDEANCR	738.94364
12	P23142	DSSCGTGYELTEDnSCK	962.373
13	P36955	VTQnLT LIEESLTSEFIHDIDR	858.77065
14	O43866	nTCNHDEDTWVECEDPFDLR	1277.01049
15	O75882	AATCINPLnGSVCERPA nHSAK	790.37348
		IDSTGnVTNELR	660.32611
		ISnSSDTVECESENWK	1023.4066
		AATCINNPLnGSVCERPA nHSAK	790.70453
		VFHIHnESWVLLTPK	607.66152
16	O95445	TELFSSSCPGGIMLnETGQGYQR	864.05387
17	P00450	DVDKEFYLFPTVFDEnESLLLEDNIR	1054.5107
		DVDKEFYLFPTVFDEnESLLLEDNIR	1581.76684
		EHEGAIYPDnTTDFQR	947.41572
		ELHHLQEQnVSNAFLDK	1011.99721
		ELHHLQEQnVSNAFLDK	1012.49873
		ELHHLQEQnVSNAFLDKGEFYIGSK	968.81557
		ELHHLQEQnVSNAFLDKGEFYIGSK	581.89005
		EnLTAPGSDSAVFFEQGTTR	709.99856
18	P00734	HQDFNSAVQLVEnFCR	693.65427
		nFTENDLLVR	611.31057
		SEGSSVnLSPPLEQCV PDR	1036.48816
		SRYPHKPEInSTTHPGADLQENFCR	591.882
		SRYPHKPEInSTTHPGADLQENFCR	986.13276
		YPHKPEInSTTHPGADLQENFCR	904.75341
		YPHKPEInSTTHPGADLQENFCR	679.06726
		MVSHHnLTTGATLINEQWLLTTAK	894.12996
		MVSHHnLTTGATLINEQWLLTTAK	894.46316
		MVSHHnLTTGATLINEQWLLTTAK	1349.19282

		MVSHHnLTTGATLINEQWLLTTAK	899.46312
		NLFLnHSEnATAK	730.36207
		NLFLnHSEnATAK	487.57228
		NLFLnHSEnATAK	731.34936
		VVLHPnYSQVDIGLIK	898.50026
		VVLHPnYSQVDIGLIK	698.73452
19	P00739	MVSHHnLTTGATLINEQWLLTTAK	894.12996
		MVSHHnLTTGATLnEQWLLTTAK	894.46316
		MVSHHnLTTGATLINEQWLLTTAK	1349.19282
		MVSHHnLTTGATLINEQWLLTTAK	899.46312
		NLFLnHSEnATAK	730.36207
		NLFLnHSEnATAK	487.57228
		NLFLnHSEnATAK	731.34936
20	P00751	IVLDPSGSMNIYLVLDGSDSIGASnFTGAK	1053.18567
		IVLDPSGSMNIYLVLDGSDSIGASnFTGAK	1033.84361
21	P01008	LGACnDTLQQLMEVFK	942.44991
		LGACnDTLQQLMEVFK	934.4502
		SLTFnETYQDISELVYGAK	1090.0256
22	P01009	ADTHDEILEGLNFnLTEIPEAQIHEGFQELLR	1231.93956
		ADTHDEILEGLNFnLTEIPEAQIHEGFQELLR	1231.60789
		ITPNLAFAFSLYRQLAHQSnSTNIFFSPVSIATAFAML SLGTK	1202.37227
		QLAHQSnSTNIFFSPVSIATAFAMLSLGTK	1061.54552
		ITPNLAFAFSLYRQLAHQSnSTNIFFSPVSIATAFAML SLGTK	1206.36247
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		LSSWVLLMKYLGnATAIFFLPDEGK	938.8295
		YLGnATAIFFLPDEGK	878.94304
		QLAHQSnSTNIFFSPVSIATAFAMLSLGTK	1066.87599
		ITPNLAFAFSLYRQLAHQSnSTNIFFSPVSIATAFAML SLGTK	1202.1147
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23	P01011	FnLTETSEAEIHQS FQHLLR	801.0701
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		SLGNVnFTVSAEALSEQELCGTEVPSVPEHGR	1138.87752
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25	P01042	LNAENnATFYFK	716.83907
		LNAENnATFYFK	717.33644
		YNSQnQSNNQFVLYR	938.42978
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		ITYSIVQTnCSK	707.84779
26	P01591	EnISDPTSPLR	615.30434
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		VPGnVTAVLGETLK	699.89363
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		YKnNSDISSTR	429.53363
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		GLTFQqNASSMCVPDQDTAIR	1178.52982
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41	P02766	ALGISPFHEHAEVVFTAnDSGPR	856.08875
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43	P02787	LCMGSGLnLCEPNNK	854.87853
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44	P02790	ALPQPQnVTSLLGCTH	579.62651
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		IYSGILnLSDITK	719.39565
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		LSVDKDQYVEPEnVTIQCDSGYGVVGPQSITCSGnR	1325.27129
47	P04004	NnATVHEQVGGPSLTSDLQAQSK	1192.06854
		NnATVHEQVGGPSLTSDLQAQSK	1191.58363
48	P04070	EVFVHPnYSK	407.53701
49	P04114	FVEGSHnSTVSLTTK	804.39888

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		VNQNLVYESGSLnFSK	900.44342
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		FnSSYLQGTNQITGR	844.39967
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		VNQNLVYESGSLnFSK	600.63267
50	P04196	VIDFnCTTSSVSSALANTK	1008.48308
		VIDFnCTTSSVSSALANTK	1008.97393
51	P05090	ADGTVNQIEGEATPVnLTEPAK	1128.05398
		ADGTVnQIEGEATPVnLTEPAK	1128.55581
		ADGTVNQIEGEATPVnLTEPAKLEVK	1362.69193
		ADGTVNQIEGEATPVnLTEPAKLEVK	1363.20163
52	P05155	AKVGQLQLSHnLSLVILVPQNLK	629.12951
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		DTFVnASR	455.7166
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		VLSnNSDANLELINTWVAKNTNNK	911.12845
		VLSnNSDANLELINTWVAKNTNNK	910.7944
53	P05156	ACDGIhDCGDQSDELCK	1087.89389
		FLNnGTCTAEGK	657.28922
		FLNnGTCTAEGK	656.7951
		LSDLSInSTECLHVVHCR	681.31764
54	P05543	TLYETE VFSTDFSnISAAK	1062.50019
		VTACHSSQPnATLYK	559.93472
55	P06276	DnNSIITR	467.2349
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		YGNPnETQNNSTSWPVFK	1042.96303
		WSDIWnATK	561.26634
		EnETEIIK	488.74454
56	P06681	LTDITCGVGnMSAnASDQER	733.31532
		LGSYPVGnVSFECEDGFILR	1159.03814
57	P07996	VVnSTTGPEHLR	456.56839
58	P08185	AVLQLNEEGVDTAGSTGVTLnLTSKPIILR	1037.57012
		AVLQLNEEGVDTAGSTGVTLnLTSKPIILR	1037.90373
		AQLLQGLGFnLTER	809.43073
59	P08603	IPCSQPPQIEHGTInSSR	1011.48744
		MDGASnVTCINSR	770.33009
		SPDVInGSPISQK	671.84675
		ISEEnETTCYMGK	781.82116
		SPYEMFGDEEVMCLNGnWTEPPQCK	1045.42356

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		FSDGLESnSSTQFEVK	888.40321
		GLnVTLSSSTR	553.29629
61	P0C0L5	nTTCQDLQIEVTVK	825.4084
		FSDGLESnSSTQFEVK	888.40321
		GLnVTLSSSTR	553.29629
62	P0DOX2	HYTnSSQDVTVPCT	832.86967
		TPLTAnITK	480.27343
		LSLHRPALEDLLLGEAnLTCTLTGLR	988.86513
63	P0DOX3	TLLnASR	388.21919
64	P0DOX5	EEQYnSTYR	595.7516
		EEQYnSTYRVVSVLTVLHQDWLNGK	994.16448
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		TKPREEQYnSTYR	596.28829
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		GLTFQqASSMCVPDQDTAIR	1170.53085
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		MLnTSSLLEQLNEQFNWVSR	1214.0856
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		LAnLTQGEDQYYLR	842.91311
69	P13671	VLnFTTK	412.2319
		YYQEnFCEQICKS	885.36973
		KLECNGEnDCGDNSEDR	1006.88
70	P14151	DnYTDLVAIQNK	697.84338
71	P17936	GLCVnASAVSR	567.78108
72	P19652	SVQEIQATFFYFTpNKTEDTIFLR	966.14946
		QNQCFYnSSYLNVQR	961.42723
		QnQCFYnSSYLNVQR	961.92936
73	P19823	GAFISnFSMTVDGK	737.84655
74	P19827	ICDLLVANNNHFAHFFAPQnLTNMNK	598.29416
75	P20851	EWDnTTTECR	656.75964
		LGHCpDPVLVNGEFSSSGPVnVSDK	871.41639
		LGHCpDPVLVNGEFSSSGPVnVSDK	871.74642
76	P22792	LYLGSNnLTALHPALFQnLSK	772.74542
		LYLGSNnLTALHPALFQnLSK	773.07922
		AFGSNPnLTK	525.26657

77	P25311	DIVEYYnDSnGSHVLQGR	689.65163
		DIVEYYnDSnGSHVLQGR	1034.46731
78	P27169	HAnWTLTPLK	591.31893
		VTQVYAEnGTVLQGSTVASVYK	1158.09097
		VVAEGFDFANGInISPDGK	976.47218
79	P29622	DFYVDEnTTVR	680.30647
		SQILEGLGFnLTELSESDVHR	782.3979
80	P43251	NPVGLIGAEnATGETDPSHSK	699.00239
		FnDTEVLQR	561.77605
81	P43652	DIENFnSTQK	598.77512
		DIENFnSTQK	599.26674
		nCCNTENPPGCYR	821.80796
		YAEDKFnETTEK	738.33005
82	P49908	EGYSnISYIVVNHQGISSR	708.68197
83	P51884	LGSFEGLVnLTFIHLQHNR	732.72259
		LHINHNNLTESVGPLPK	628.67094
84	P55058	VSnVSCQASVSR	647.8067
85	Q03591	LQNNENnISCVER	796.36091
		LQNNENnISCVER	795.86277
		SPYEMFGDEEVMCLNGnWTEPPQCK	1045.09531
		SPYEMFGDEEVMCLNGnWTEPPQCK	1045.42557
86	Q08380	AAIPSALDTnSSK	638.3251
		GLnLTEDTYKPR	469.90968
		DAGVVCTnETR	611.77189
		ALGFEnATQALGR	674.84647
87	Q12805	TCQDInECETTNECR	965.87233
88	Q14624	LPTQnITFQTESSVAEQAEFQSPK	1405.67
89	Q8TBF5	nITEAVMVSENFIEAPNYLSK	867.08523
90	Q96PD5	GFGVAIVGnYTAALPTEAALR	1046.56621
		LEPVHLQLQCMSQEQLAQVAAnATK	936.80694
91	Q9HC56	SSTAKVTINVMVDNDNSPVVISPPSnTSFK	1069.87227
92	Q9UK55	ETFFnLSK	493.74497
93	Q9Y6R7	ANQQLnFTEAK	632.81295
94	P41222	WFSAGLASnSSWLR	791.89195
95	P03951	LETTVnYTDSQRPICLPSK	741.70402

Table S3. Comparison results of enrichment performance between ZIF-8/SAP and other reporting materials.

Material	Number of glycopeptides enriched from HRP	Binding capacity (mg/g)	Water contact angles	Sample	Glycopeptides / Glycoproteins	Ref.
MUio-66-NH ₂ /PA	21	40	-	human serum 10 µL	101/48	[1]
magG/PDA/Au/L-Cys	14	-	-	human serum 2 µL	40/31	[2]
Ti-MOF	17	250	43.6°	human serum 2 µL	66/41	[3]
Hf-BTB	25	250	34°	human serum 2 µL	78/29	[4]
magMOF@Au-maltose	24	83	15.9°	human serum 1 µL	113/46	[5]
TpPa-1@Ag@GSH	31	160	-	human serum 10 µL	223/-	[6]
GO-PEI-Carr	-	-	-	human serum 2 µL	76/56	[7]
SBA-15-NH ₂	-	-	-	human serum 5 µL	77/56	[8]
TpPa-1	22	178	-	human serum 10 µL	128/70	[9]
ZIF-8/SAP	35	300	13°	human serum 10 µL	283/95	This work

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