

1 **Supporting information**
2 **Hydrophilic tripeptide-functionalized magnetic**
3 **metal–organic frameworks for highly efficient**
4 **enrichment of N-linked glycopeptide**

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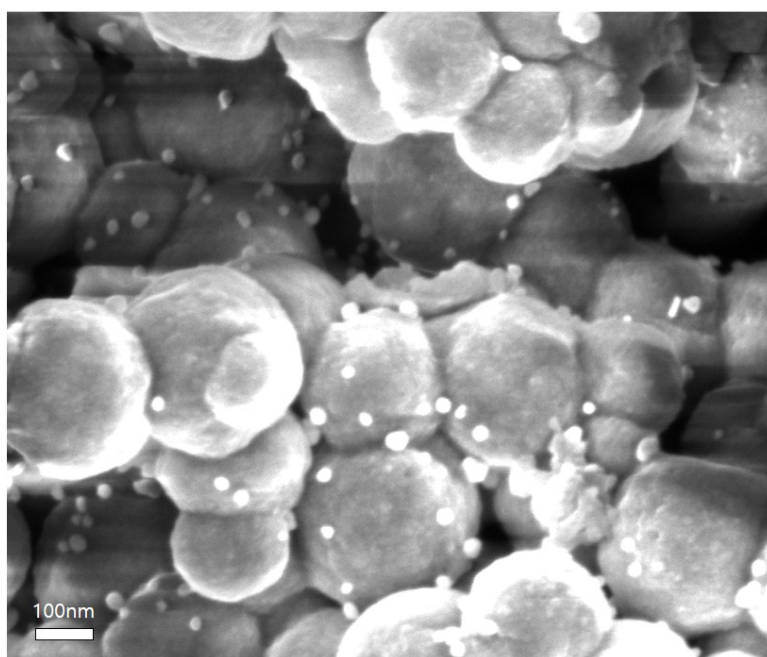
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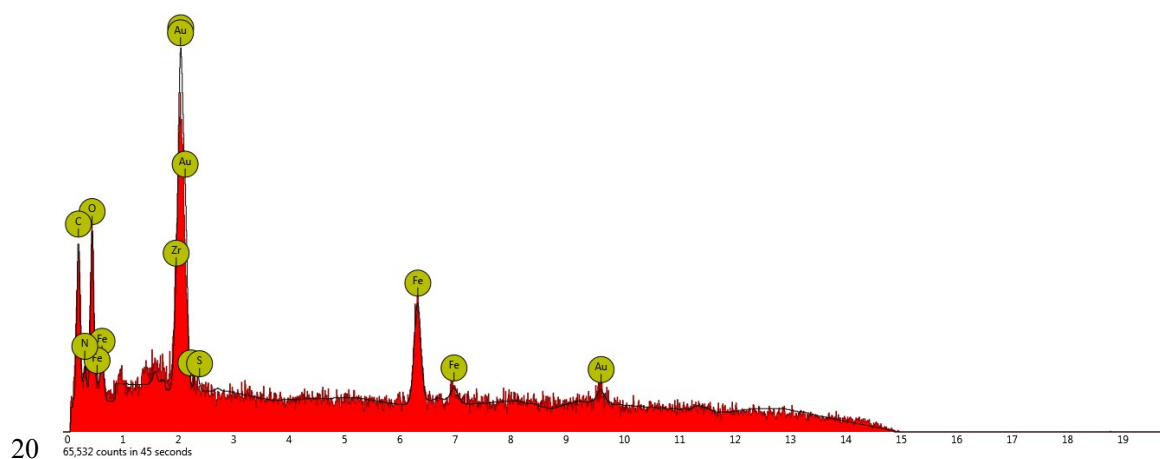
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18 **Fig S1.** SEM image of mMOF@Au@GSH nanocomposites.

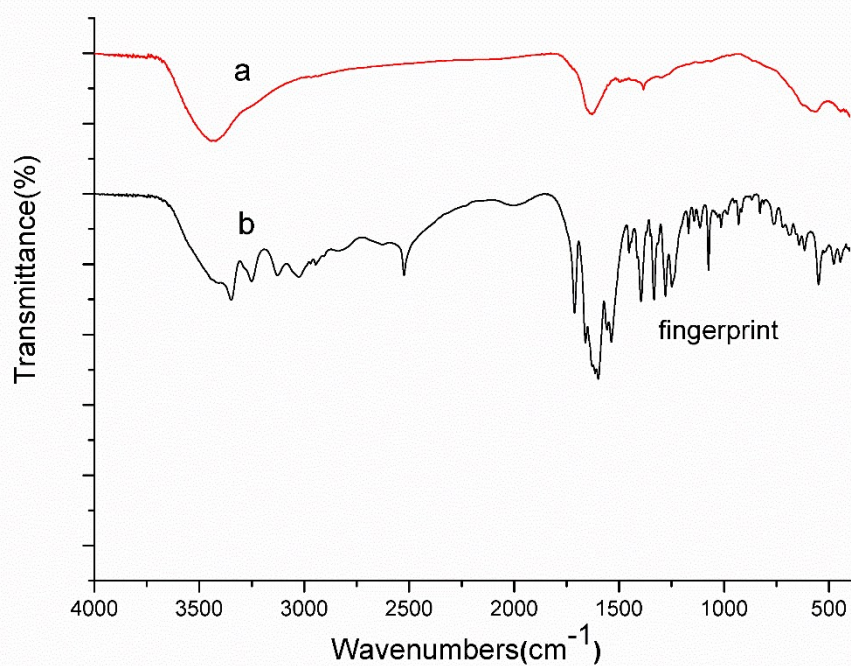
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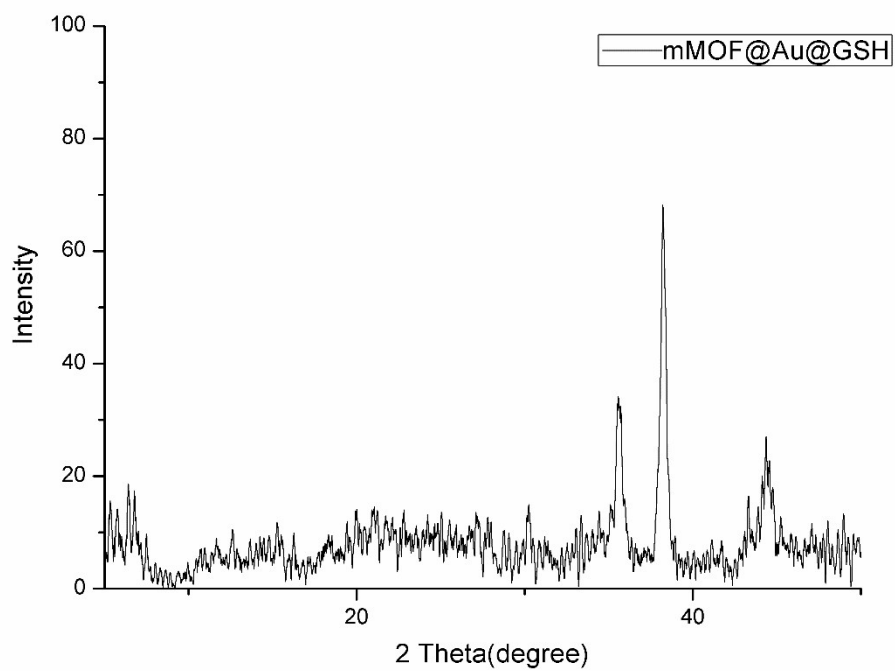
Element Symbol	Atomic %	Weight %
Au	52.21	92.46
C	26.60	2.87
O	11.54	1.66
N	5.73	0.72
Fe	2.25	1.13
Zr	1.26	1.04
S	0.41	0.12

21 **Fig S2.** The energy dispersive X-ray (EDX) spectrum of mMOF@Au@GSH.

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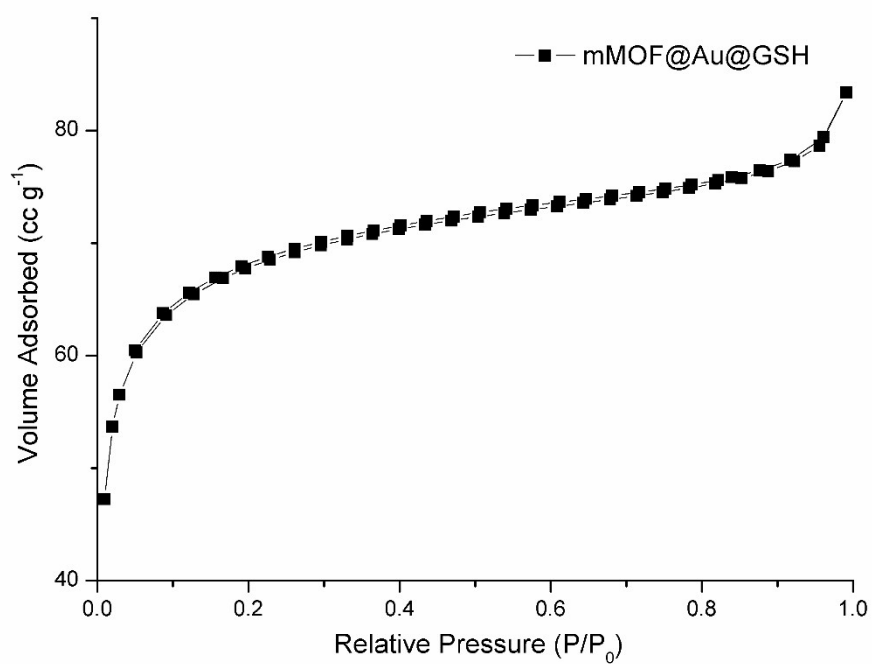


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24 **Fig S3.** The FTIR spectra of (a) mMOF@Au and (b) mMOF@Au@GSH
25 nanomaterials.
26



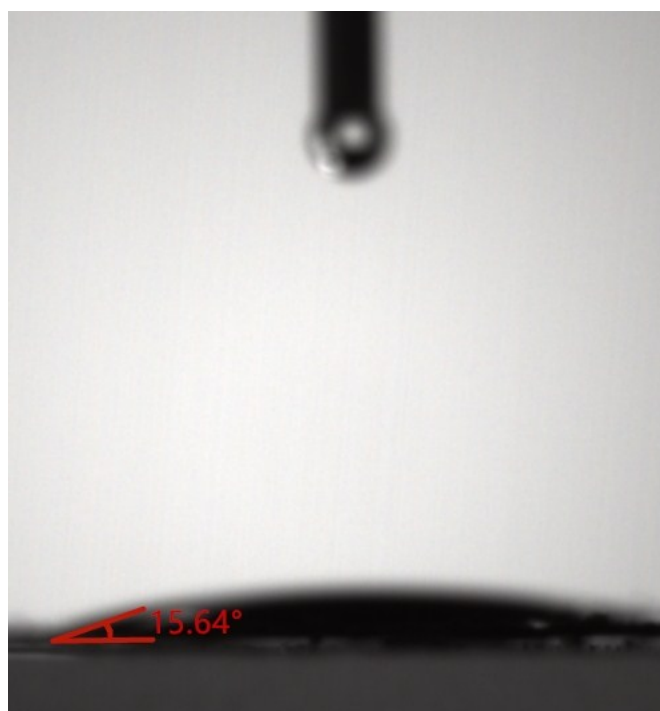
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28 **Fig S4.** Wide angle XRD pattern of mMOF@Au@GSH nanomaterials.



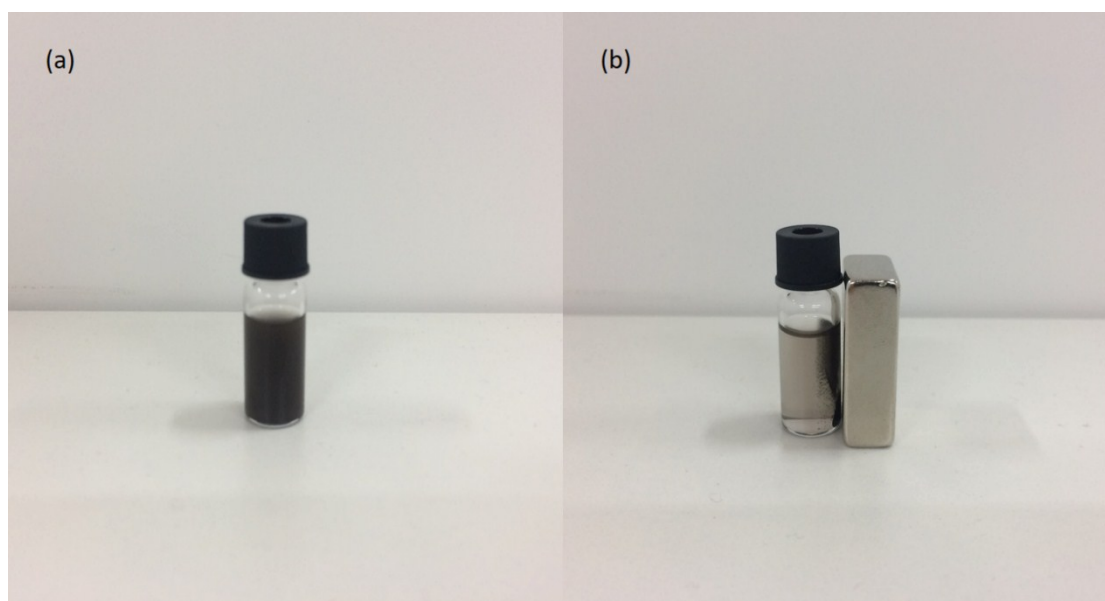
30
31 **Fig S5.** N_2 adsorption-desorption isotherm of mMOF@Au@GSH nanomaterials
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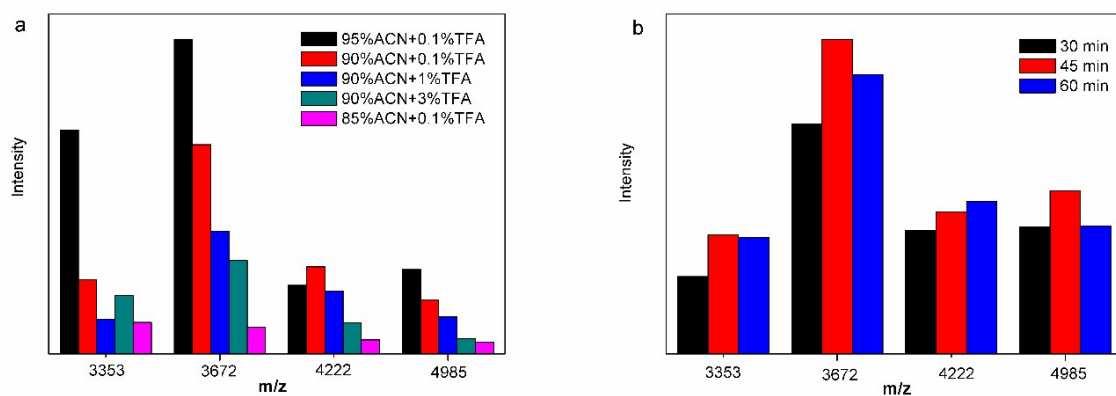


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35 **Fig S6.** Water contact angle of mMOF@Au@GSH nanomaterials.



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37 **Fig S7.** mMOF@Au@GSH nanomaterials dispersed in water (a) and separated
38 magnetically in five seconds (b).
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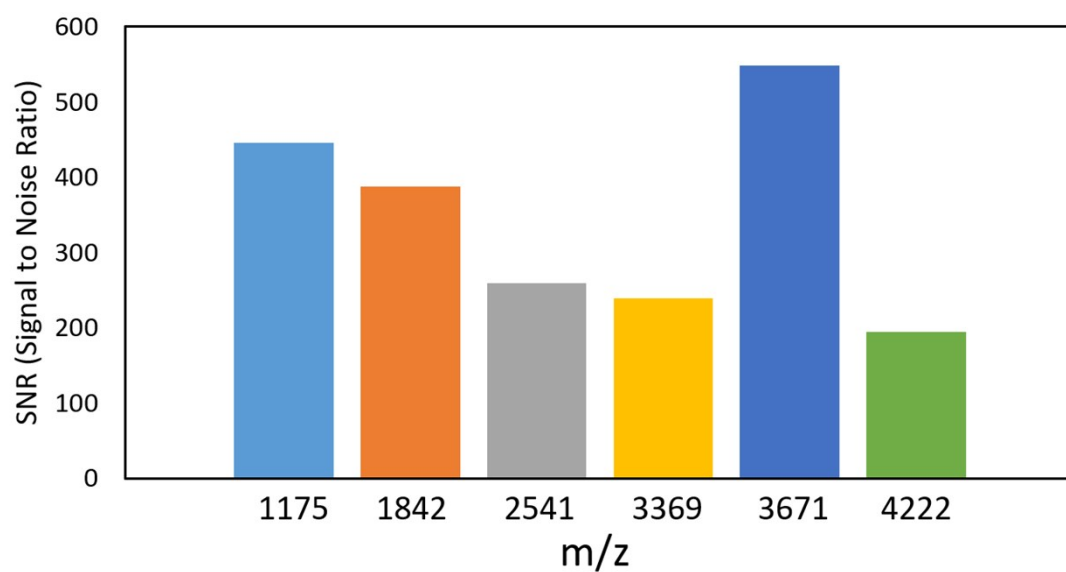


43
 44 **Fig S8.** Peak intensities of four selected glycopeptides enriched by mMOF@Au@GSH
 45 nanocomposites: (a) in different loading buffer; (b) with different incubation duration.
 46

47 **Table S1.** Detail information of the glycopeptides enriched from HRP tryptic digest by
 48 using mMOF@Au@GSH. N#: N-glycosylation site.

No	Observed m/z	Glycan composition	Amino acid sequence
H1	1842.5	XylMan ₃ FucGlcNAc ₂	NVGLN#R
H2	2541.0	XylMan ₃ FucGlcNAc ₂	SSPN#ATDTIPLVR
H3	2590.8	XylMan ₃ FucGlcNAc ₂	PTLN#TTYLQTLR
H4	2610.8	XylMan ₃ GlcNAc ₂	MGN#ITPLTGTQGQIR
H5	2850.4	FucGlcNAc	GLIQSDQELFSSPN#ATDTIPLVR
H6	3222.4	Man ₃ FucGlcNAc ₂	SFAN#STQTFNFNAFVEAMDR
H7	3321.1	XylMan ₃ FucGlcNAc ₂	QLTPTFYDNPCPN#VSNIVR
H8	3353.0	XylMan ₃ FucGlcNAc ₂	SFAN#STQTFNFNAFVEAMDR
H9	3369.0	XylMan ₃ FucGlcNAc ₂	SFAN#STQTFNFNAFVEAM*DR
H10	3508.7	XylMan ₂ FucGlcNAc ₂	GLIQSDQELFSSPN#ATDTIPLVR
H11	3526.2	XylMan ₃ GlcNAc ₂	GLIQSDQELFSSPN#ATDTIPLVR
H12	3539.6	Man ₃ FucGlcNAc ₂	GLIQSDQELFSSPN#ATDTIPLVR
H13	3671.3	XylMan ₃ FucGlcNAc ₂	GLIQSDQELFSSPN#ATDTIPLVR
H14	3895.1	XylMan ₃ FucGlcNAc ₂	LHFHDCFVNGCDASILDN#TTSFR
H15	4221.4	XylMan ₃ FucGlcNAc ₂	QLTPTFYDNPC(AAVESACPR)PN#VSNIV R
H16	4820.6	XylMan ₂ FucGlcNAc ₂ , XylMan ₂ GlcNAc ₂	LYN#FSNTGLPDPTLN#TTYLQTLR
H17	4837.9	XylMan ₃ FucGlcNAc ₂ , XylMan ₃ GlcNAc ₂	LYN#FSNTGLPDPTLN#TTYLQTLR
H18	4852.7	Man ₃ FucGlcNAc ₂ , XylMan ₃ FucGlcNAc ₂	LYN#FSNTGLPDPTLN#TTYLQTLR
H19	4984.7	XylMan ₃ FucGlcNAc ₂ , XylMan ₃ FucGlcNAc ₂	LYN#FSNTGLPDPTLN#TTYLQTLR

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53 **Fig. S9** The S/N ratio of maltoheptaose ($[M+Na]^+ = 1175$ Da) and glycopeptides
 54 derived from HRP after enrichment by mMOF@Au@GSH nanoparticles in parallel
 55 tests.

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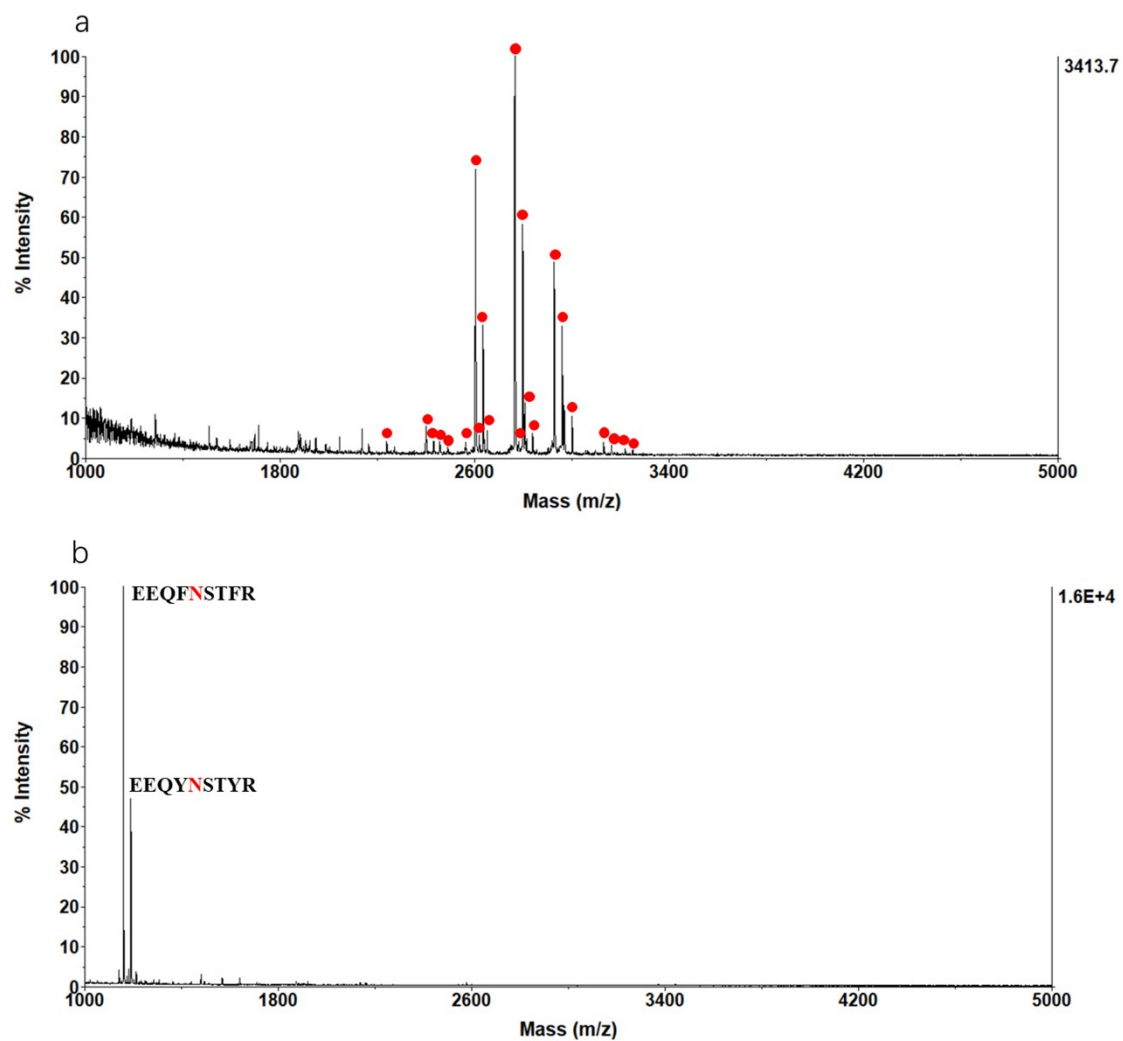
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58 **Table S2** Recovery of six selected glycopeptides from IgG digest

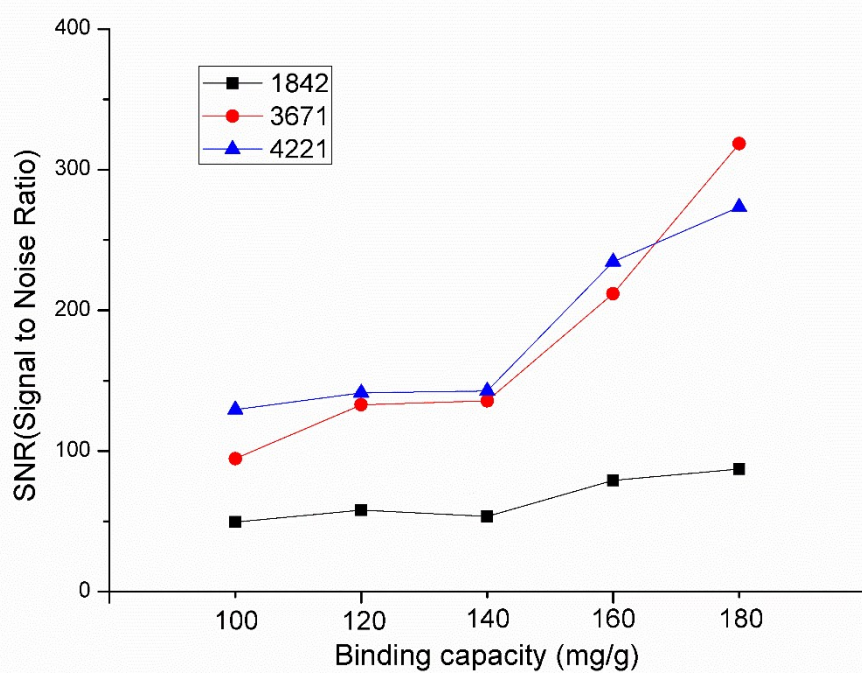
m/z	Recovery±S.D. (% , n=3)
1842	85.3±2.1
2541	81.2±4.3
3369	84.5±2.6
3671	79.8±4.5
4222	87.3±3.7

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 62 **Fig. S10** MALDI-TOF MS spectra of 1.0 pmol/ μ L digest of IgG glycoprotein: (a) the
 63 eluent after enrichment and (b) the eluent deglycosylated by PNGase F.
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 66 **Fig. S11.** The S/N ratio of glycopeptides derived from HRP in supernatant after
 67 enrichment by mMOF@Au@GSH nanoparticles.
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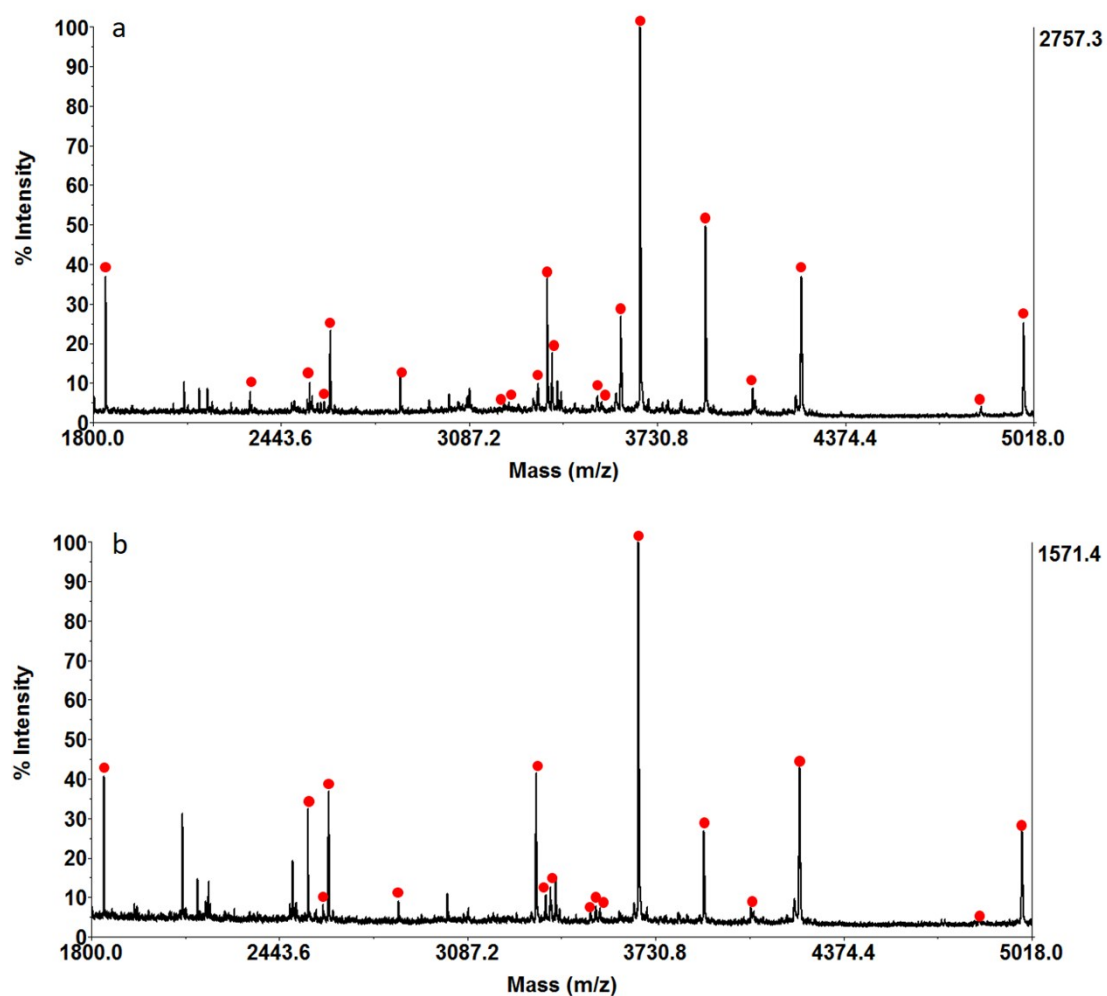
70 **Table S3.** Detail information of the glycopeptides enriched from IgG digestion by
 71 using mMOF@Au@GSH. N#: N-glycosylation site.

No.	Observed m/z	Glycan composition	Amino acid sequence
I1	2236.7	[Hex]3[HexNAc]2[Fuc]1	EEQFN#STFR
I2	2284.6	[Hex]3[HexNAc]3	EEQYN#STYR
I3	2399.7	[Hex]3[HexNAc]3[Fuc]1	EEQFN#STFR
I4	2431.7	[Hex]3[HexNAc]3[Fuc]1	EEQYN#STYR
I5	2455.7	[Hex]3[HexNAc]4	EEQFN#STFR
I6	2488.7	[Hex]3[HexNAc]4	EEQYN#STYR
I7	2561.8	[Hex]4[HexNAc]3[Fuc]1	EEQFN#STFR
I8	2593.7	[Hex]4[HexNAc]3[Fuc]1	EEQYN#STYR
I9	2602.8	[Hex]4[HexNAc]4[Fuc]1	EEQFN#STFR
I10	2618.8	[Hex]4[HexNAc]4[Fuc]1, or[Hex]4[HexNAc]4	EEQFN#STYR, or EEQFN#STFR
I11	2634.8	[Hex]4[HexNAc]4[Fuc]1,or [Hex]4[HexNAc]4	EEQYN#STYR, or EEQFN#STYR,
I12	2650.7	[Hex]4[HexNAc]4	EEQYN#STYR
I13	2656.7	[Hex]3[HexNAc]5	EEQFN#STFR
I14	2764.8	[Hex]4[HexNAc]4[Fuc]1	EEQFN#STFR
I15	2780.8	[Hex]4[HexNAc]4[Fuc]1,or [Hex]5[HexNAc]4	EEQFN#STYR, or EEQFN#STFR
I16	2796.8	[Hex]4[HexNAc]4[Fuc]1,or [Hex]5[HexNAc]4	EEQYN#STYR, or EEQFN#STYR
I17	2805.8	[Hex]3[HexNAc]5[Fuc]1	EEQFN#STFR
I18	2812.8	[Hex]5[HexNAc]4	EEQYN#STYR
I19	2820.8	[Hex]3[HexNAc]5[Fuc]1, or [Hex]4[HexNAc]5	EEQFN#STYR, or EEQFN#STFR
I20	2837.8	[Hex]3[HexNAc]5[Fuc]1, or [Hex]4[HexNAc]5	EEQYN#STYR or EEQFN#STYR
I21	2926.8	[Hex]5[HexNAc]4[Fuc]1	EEQFN#STFR
I22	2958.8	[Hex]5[HexNAc]4[Fuc]1	EEQYN#STYR
I23	2967.9	[Hex]4[HexNAc]5[Fuc]1	EEQFN#STFR
I24	2999.9	[Hex]4[HexNAc]5[Fuc]1,or [Hex]5[HexNAc]5	EEQYN#STYR, or EEQFN#STYR
I25	3056.8	[Hex]4[HexNAc]4[Fuc]1[NeuAc]1	EEQFN#STFR
I26	3128.9	[Hex]5[HexNAc]5[Fuc]1	EEQFN#STFR
I27	3161.0	[Hex]5[HexNAc]5[Fuc]1	EEQFN#STYR

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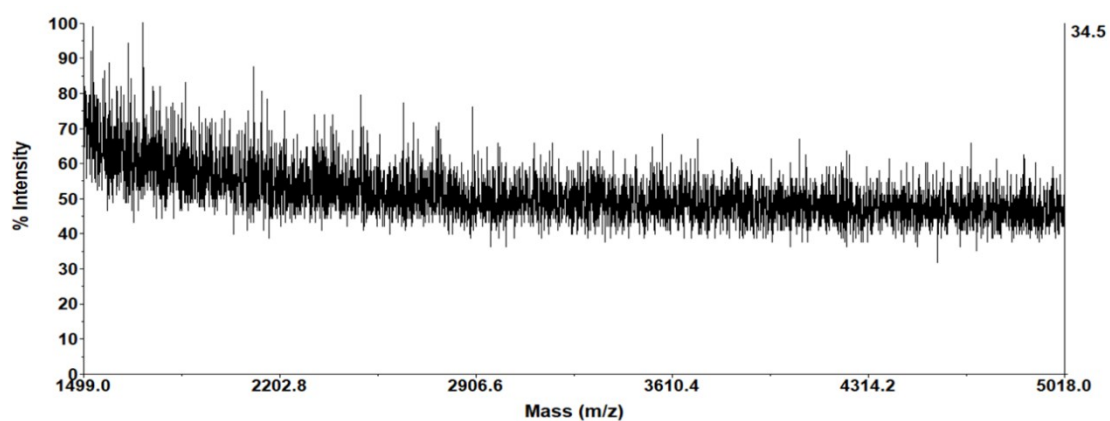
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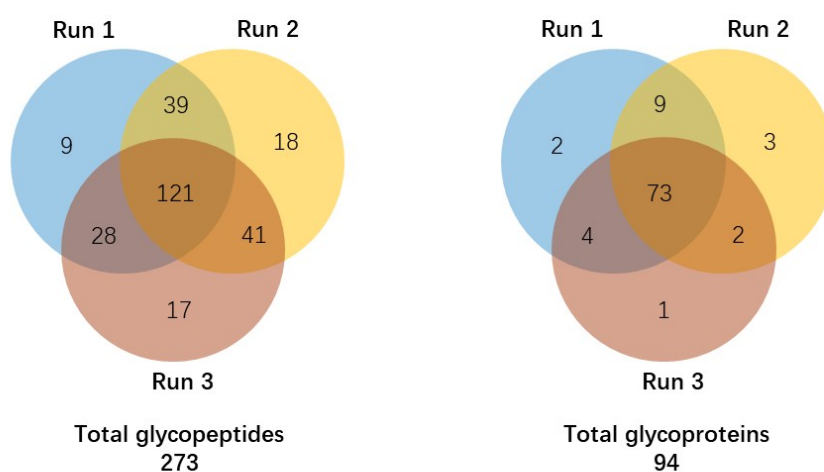


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76 **Fig S12.** MALDI mass spectra of HRP digests after enrichment with the same
 77 mMOF@Au@GSH nanomaterials (a) for the first time and (b) for the fifth time



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80 **Fig. S13.** MALDI mass spectra of washing eluent of mMOF@Au@GSH nanomaterials
81 for the third time.
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83
84 **Fig. S14.** Reproducibility evaluation of mMOF@Au@GSH based enrichment of
85 human serum, identified deglycosylated N-glycopeptide.

87 **Table S4.** Detail information of the glycopeptides enriched from tryptic digests of
88 human serum by mMOF@Au@GSH nanomaterials. n: N-glycosylation site.

No.	Sequence	Protein Group Accessions
1	YTGnASALFILPDQDK	P01011
2	YPHKPEInSTTHPGADLQENFcR	P00734
3	YPHKPEInSTTHPGADLQEnFcR	P00734
4	YNSQnQSNNQFVLYR	P01042
5	YNSQnQSnNQFVLYR	P01042
6	YNSQnQSnNQFVLYR	P01042
7	YLGnATAIFFLPDEGK	P01009
8	YKnNSDISSTR	P01871
9	YDFnSSmLYSTAK	P04114
10	YAEDKFnETTEK	P43652
11	WVSnKTEGR	P01008
12	VYSGILnQSEIK	P03951
13	VYKPSAGnNSLYR	P02749
14	VVnSTTGPGEHLR	P07996
15	VVnNSPQPQNVVFDVQIPK	P19823
16	VVLHPnYSQVDIGLIK	P00738
17	VVLHPnYSQVDIGLIK	P00738
18	VVGVPYQGnATALFILPSEGK	P05154
19	VTQVYAEnGTVLQGSTVASVYK	P27169
20	VTQnLTLIEESLTSEFIHDIDR	P36955
21	VTAcHSSQPnATLYK	P05543
22	VSnVScQASVSR	P55058
23	VSnQTLSLFFTVLQDVPVR	P01023
24	VScPIMPcSnATVPDGEccPR	P07996
25	VNQNLVYESGSLnFSK	P04114
26	VnESVVSIAAQK	Q13201
27	VLSnNSDANLELINTWVAK	P05155
28	VLnFTTK	P13671
29	VGQLQLSHnLSLVILVPQNLK	P05155
30	VcQDcPLLAPLnDTR	P02765
31	TVLTPATnHMGnVTFTIPANREFK	P01024
32	TVLTPATNHMGnVTFTIPANR	P01024
33	TVLTPATnHMGnVTFTIPANR	P01024
34	TVLTPATnHMGnVTFTIPAnR	P01024
35	TVLTPATNHmGnVTFTIPANR	P01024
36	TPLTAnITK	P01877
37	TmFPnLTDVR	P06681
38	TLnQSSDELQLSMGNAMFVK	P01011
39	TLnQSSDELQLSMGnAMFVK	P01011

40	TLFc _n ASK	P20851
41	TKPREEQY _n STYR	P01857
42	TKPREEQY _n STFR	P01860
43	TKPREEQF _n STYR	P01861
44	TKPREEQF _n STFR	P01859
45	TIDDLK _n QIL _n LTTDNANILLQIDNAR	P13645
46	THT _n ISESHPh _n ATFSAVGEASlcEDDWNSGER	P01871
47	THT _n ISESHPh _n ATFSAVGEASlcEDDW _n SGER	P01871
48	TEVSSNHVLIYLDKVS _n QTL _n SLFFTVLQDVPVR	P01023
49	TELFSSScPGGIML _n ETGQGYQR	O95445
50	SVVAPATDGGL _n LSTFLR	P41222
51	SVQEIQATFFYFTPh _n KTEDTIFLR	P02763;P19652
52	SRYPHKPEIn _n STTHPGADLQENFcR	P00734
53	SQILEGLGF _n LTESESDVHR	P29622
54	SPDVIn _n GSPISQK	P08603
55	SLTF _n ETYQDISELVYGAK	P01008
56	SLPNFPh _n TSATAn _n ATGGR	Q6UXB8
57	SLG _n V _n FTVSAEALESQELcGTEVPSVPEHGRK	P01023
58	SLG _n V _n FTVSAEALESQELcGTEVPSVPEHGR	P01023
59	SEGSSV _n LSPPLEQcVPDRGQQYQGR	P00734
60	SEGSSV _n LSPPLEQcVPDR	P00734
61	RnHScEPcQTLAVR	P00748
62	QQQHLFGS _n VTDeSGNFcLFR	P02787
63	QnQcFY _n SSYLN _n VQREnGTVSR	P19652
64	QNQcFY _n SSYLN _n VQR	P19652
65	QLVEIEKVVLHP _n YSQVDIGLIK	P00738
66	QLVEIEKVVLHP _n YSQVDIGLIK	P00738
67	QLAHQS _n STNIFFSPVSIATAFAMLSLGTK	P01009
68	QLAHQS _n ST _n IFFSPVSIATAFAMLSLGTK	P01009
69	QLAHQS _n ST _n IFFSPVSIATAF _n AMLSLGTK	P01009
70	QKDVDKEFYLFPTVFDE _n ESLLEDNIR	P00450
71	QINSYVK _n KTQ GK	P08185
72	QDQcIY _n TTYLN _n VQREnGTISR	P02763
73	QDQcIY _n TTYL _n VQREnGTISR	P02763
74	PALEDLLLGSEAn _n L _n TcTLTGLR	P01876;P01877
75	nYTLTGR	P10643
76	nVSTGDVN _n EmNAAPGVDLTQLLNMR	P13645
77	NVIFSPLSISTALAFSLGAH _n TTLTEILK	P01011
78	nTTcQDLQIEVTVK	P0C0L4
79	nPVGLIGAEn _n ATGETDPSHSK	P43251
80	nNSDISSTR	P01871
81	NnATVHEQVGGPSLTSDLQAQSK	P04004
82	nnATVHEQVGGPSLTSDLQAQSK	P04004

83	nLTSLTESVDR	P80108
84	nLSMPLLPADFHK	P05546
85	NLFLnHSEnATAKDIAPTLTLYVGKK	P00739;P00738
86	nLFLnHSEnATAKDIAPTLTLYVGKK	P00739;P00738
87	NLFLnHSEnATAK	P00739;P00738
88	NLFLnHSEnATAK	P00739;P00738
89	nLFLnHSEnATAK	P00739;P00738
90	nISDGFDPDNDVAALALPAHSYSGR	P04004
91	NInYTER	P80108
92	nHScSEGQISIFR	O75882
93	nHScEPcQTLAVR	P00748
94	nGTLVAFR	Q92954
95	nGTGHGnSTHHGPEYMR	P02790
96	nGTGHGnSTHHGPEYmR	P02790
97	nFTENDLLVR	P00734
98	nATLVnEADKLR	P15144
99	nAHGEEKEnLTAR	Q06033
100	MVSHHnLTTGATLINEQWLLTTAK	P00739;P00738
101	MVSHHnLTTGATLInEQWLLTTAK	P00739;P00738
102	mVSHHnLTTGATLINEQWLLTTAK	P00739;P00738
103	mVSHHnLTTGATLInEQWLLTTAK	P00739;P00738
104	MnKTVAVR	P01024
105	MLnTSSLLEQLNEQFNWVSR	P10909
106	MLnTSSLLEQLnEQFNWVSR	P10909
107	mLnTSSLLEQLNEQFNWVSR	P10909
108	mLnTSSLLEQLnEQFNWVSR	P10909
109	MDGASnVTcINSR	P08603
110	MDGASnVTcInSR	P08603
111	LYLGSnNLTALHPALFQnLSK	P22792
112	LYLGSnNLTALHPALFQnLSK	P22792
113	LYLGSnNLTALHPALFQnLSK	P22792
114	LVPHMnVSAVEK	Q96KN2
115	LVLSEKTVLTPATNHMGnVTFTIPANREFK	P01024
116	LVLSEKTVLTPATnHMGnVTFTIPAnREFK	P01024
117	LVLSEKTVLTPATnHmGnVTFTIPANREFK	P01024
118	LVLSEKTVLTPATNHMGnVTFTIPANR	P01024
119	LSVDKDQYVEPEnVTIQcDSGYGVVGPOSITcSGnR	P04003
120	LSLHRPALEDLLLGEAnLTcTLTGLR	P01876;P01877
121	LSDLInSTEcLHVHcR	P05156
122	LQNNEnnIScVER	P36980
123	LQnNEnnIScVER	P36980
124	LQnLTLPTnASIK	Q13201
125	LQAPLnYTEFQKPIcLPSK	P03952

126	LPTQnITFQTESSVAEQAEFQSPK	Q14624
127	LnAENnATFYFK	P01042
128	LNAEnnATFYFK	P01042
129	LINDYVKnGTR	P01011
130	LHEITnETFR	Q6EMK4
131	LGSFEGLVnLTFIHLQHNR	P51884
132	LGnWSAMPScK	P02749
133	LGnWSAmPScK	P02749
134	LGHcPDPVLVNGEFSSGPVnVSDK	P20851
135	LGAcnDTLQQLMEVFKFDTISEK	P01008
136	LGAcnDTLQQLMEVFK	P01008
137	LGAcnDTLQQLmEVFK	P01008
138	LFGDKSLTFnETYQDISELVYGAK	P01008
139	LETTVnYTDSQRPIcLPSK	P03951
140	LEPVHLQLQcMSQEQLAQVAAnATK	Q96PD5
141	LDAPTNLQFVnETDSTVLVR	P02751
142	LDAPTnLQFVnETDSTVLVR	P02751
143	LcDnLSTK	P02774
144	LAnLTQGEDQYYLR	P10909
145	LAGKPTHVnVSVVMAEVDGTcY	P01876
146	KYnSQnQSNNQFVLYR	P01042
147	KYnSQnQSNnQFVLYR	P01042
148	KVcQDcPLLAPLnDTR	P02765
149	KTLFcnASK	P20851
150	KLVLSSSEKTVLTPATNHMGnVTFTIPANR	P01024
151	KLVLSSSEKTVLTPATnHMGnVTFTIPANR	P01024
152	KLPPGLLAnFTLLR	P02750
153	KLINDYVKnGTR	P01011
154	KKEDALnETR	P10909
155	KEDALnETR	P10909
156	KANQQLnFTEAK	Q9Y5Y7
157	IYSnHSALESLALIPLQAPLK	P55058
158	IYSGILnLSDITK	P03952
159	IYPGVDFGGEELnVTFVK	P03952
160	ISnSSDTVcEcEcSENWK	O75882
161	ISEEnETTcYMGK	P08603
162	ISEEnETTcYmGK	P08603
163	IPcSQPPQIEHGTInSSR	P08603
164	ILRQQQHLFGSnVTDcSGNFcLFR	P02787
165	IIVPLNNREnISDPTSPLR	P01591
166	IIPSnNSGTFR	O00533
167	IDSTGnVTNELR	O75882
168	HYTnSSQDVTVPcRVPPPPcHPR	P0DOX2

169	HnSTGeLR	P10909
170	HnFSHccSK	P43652
171	HAnWTLTPLK	P27169
172	GVTSVSQIFHSPDLAIRDTFVnASR	P05155
173	GVNFnVSK	P03952
174	GTAAnTTTAGVPcQR	P26927
175	GLTFQQnASSMcVPDQDTAIR	P01871
176	GLTFQQnASSmcVPDQDTAIR	P01871
177	GLQPTLTnPGEcRPnFTcAcR	P04275
178	GLnVTLSSSTGR	P0C0L4
179	GLnLTEDTYKPR	Q08380
180	GLcVnASAVSR	P17936
181	GINYnSSVAK	P03951
182	GHVnITR	P00734
183	GFGVAIVGnYTAALPTEAALR	Q96PD5
184	GcVLLSYLnETVTVSASLESVR	P01023
185	GAFISnFSMTVDGK	P19823
186	GAFISnFSmTVDGK	P19823
187	FVQAICeGDDcQPPAYTYnnITcASPPEVVGLDLR	P35858
188	FVGTPEVnQTTLYQR	P01033
189	FVEGSHnSTVSLTTK	P04114
190	FSDGLESnSSTQFEVKK	P0C0L4
191	FSDGLESnSSTQFEVK	P0C0L4
192	FnSSYLQGTnQITGR	P04114
193	FnSSYLQGTnQITGR	P04114
194	FnPGAESVVLsnSTLK	Q13201
195	FnLTETSEAEIHQSfQHLLR	P01011
196	FnDTEVLQR	P43251
197	FLNnGTcTAEGK	P05156
198	FLnnGTcTAEGK	P05156
199	FLnDTMAVYEAK	P29622
200	FLnDTmAVYEAK	P29622
201	FEVDSPVYnATWSASLK	P04114
202	FcRDnYTDLVAIQNK	P14151
203	EWDnTTTEcR	P20851
204	EVFVHPnYSK	P04070
205	ETFFnLSKR	Q9UK55
206	ETFFnLSK	Q9UK55
207	ESVTDHVNLIPTLEKPLQnFTLcFR	P02743
208	ESVTDHVnLIPTLEKPLQnFTLcFR	P02743
209	EnLTAPGSDSAVFFEQGTTR	P00450
210	EnISDPTSPLR	P01591
211	EnGTVSRYEGGR	P19652

212	EnGTVSR	P19652
213	EnGTISR	P02763
214	EnETEIIK	P06276
215	ELHHLQEQnVSNAFLDKGEFYIGSK	P00450
216	ELHHLQEQnVS _n AFLDKGEFYIGSK	P00450
217	ELHHLQEQnVSNAFLDK	P00450
218	ELHHLQEQnVS _n AFLDK	P00450
219	EEQYnSTYR	P01857
220	EEQYnSTFR	P01860
221	EEQFnSTYR	P01861
222	EEQFnSTFR	P01859
223	EDALnETRESETK	P10909
224	EDALnETR	P10909
225	DTLTSRPAQGVVTTLe _n VSPRR	P02751
226	DTFVnASR	P05155
227	DTAVFEcLPQHAMFGnDTITcTTHGnWTK	P02749
228	DQcIVDDITYN _{Vn} DTFHK	P02751
229	DQcIVDDITY _n V _n DTFHK	P02751
230	DnYTKAEIILSR	P06276
231	DnYTDLVAIQNK	P14151
232	DnNSIITR	P06276
233	DIVEYYNDS _n GSHVLQGR	P25311
234	DIVEYY _n DS _n GSHVLQGR	P25311
235	DIENFnSTQK	P43652
236	DIEnFnSTQK	P43652
237	DFYVDEnTTVR	P29622
238	DFVnASSK	P05546
239	DAGVVcTnETR	Q08380
240	cnYSIR	P00736
241	cIQAnYSLMENGK	P05090
242	cIQAnYSLME _n GK	P05090
243	cInQSIcEK	O75882
244	cFLGnGTGYR	Q04756
245	AYLLPAPPAPG _n ASESEEDR	P17936
246	AVnITSENLIIDVVSLIR	P02748
247	AVLQLnEEGVDTAGSTGVTL _n LTSKPIILR	P08185
248	AQLLQGLGF _n LTER	P08185
249	ANQQL _n FTEAK	Q9Y5Y7
250	AnPTVTLFPPSSEELQANK	P0DOX8
251	ALPQPQ _n VTSLLGcTH	P02790
252	ALGISPFHEHAEVVFTAnDSGPRR	P02766
253	ALGISPFHEHAEVVFTAnDSGPR	P02766
254	ALGFEnATQALGR	Q08380

255	AFITnFSMIIDGMTYPGIIK	Q14624
256	AFGSNPnLTK	P22792
257	AFEnVTDLQWLILDHNLLENSK	P51884
258	ADTHDEILEGLNFnLTEIPEAQIHEGFQELLR	P01009
259	ADTHDEILEGLnFnLTEIPEAQIHEGFQELLR	P01009
260	ADGTVNQIEGEATPVnLTEPAKLEVK	P05090
261	ADGTVnQIEGEATPVnLTEPAKLEVK	P05090
262	ADGTVNQIEGEATPVnLTEPAK	P05090
263	ADGTVnQIEGEATPVnLTEPAK	P05090
264	AATcINPLnGSVcERPAnHSAK	O75882
265	AATcInPLnGSVcERPAnHSAK	O75882
266	AAPAPQEATATFnSTADR	P13598
267	AALAAFNAQNnGSNFQLEEISR	P02765
268	AALAAFNAQNnGSnFQLEEISR	P02765
269	AALAAFNAQNnGSNFQLEEISR	P02765
270	AALAAFNAQnnGSNFQLEEISR	P02765
271	AALAAFNAQnnGSNFQLEEISR	P02765
272	AALAAFNAQnnGSnFQLEEISR	P02765
273	AAIPSALDTnSSK	Q08380

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90 **Table S5.** The number of total identified peptides and ratio of glycopeptides in human
91 serum samples.

		Peptides	Glycopeptides	Ratio	Proteins	Glycoproteins	Ratio
	Fe ₃ O ₄ @SiO ₂ -APB*	317	95	30%	103	44	42.7%
	Fe ₃ O ₄ @SiO ₂ -APB* +PMMA	358	147	41.1%	120	66	55.0%
mMOF@ Au@GSH	Run1	717	197	27.5%	134	80	59.7%
	Run2	970	219	22.6%	148	88	59.5%
	Run3	897	207	23.1%	144	87	60.4%

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94 **Table S6.** HILIC-based MOF materials for glycopeptide enrichment from human
95 serum sample

materials	human serum	glycopeptides	glycoproteins	ref.
mMOF@Au@GSH	2μL	273	94	This work
Fe ₃ O ₄ @PDA@Zr-SO ₃ H	2μL	177	85	1
MIL-101(Cr)-maltose	5μL	111	65	2
MIL-101(Cr)-NH ₂	10μL	116	42	3

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