Electronic Supplementary Material (ESI) for Nanoscale

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Supporting Information

Experimental Section

Materials and chemicals: Bovine serum albumin (BSA), 2-methylimidazole (MIM, purity 99%) and $CoCl_2 \cdot 6H_2O$ (purity 97%) were purchased from Sigma-Aldrich.Standard glycoprotein (chicken egg ovalbumin: Molecular Weight = 43 KDa, containing 386 amino acid) was obtained from Sigma-Aldrich. PNGase F (Genetimes Technology), 2, 5-dihydroxy-benzoic acid (DHB) was acquired from Sigma-Aldrich .Ultrafiltration membrane with MWCO of 10 KDa was acquired from Millipore (Bedford, MA). Polyvinylpyrrolidone (PVP， K30). Mouse brain was provided by Shanghai Second Military Medical University. All used deionized water in the experiment were prepared by Milli-Q system (Millipore, Bedford, MA).Acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany).All of other chemicals are of analytical grade .

Preparation of Co-ZIF-67 : 3.64 g of $CoCl_2 \cdot 6H_2O$ and 4.2 g PVP were dissolved in 280 ml of methanol to form a solution A, 18.41 g of 2-methylimidazole and 280 ml of methanol were mixed to form another solution B, then solution A and solution B were mingled and stirred for 15 min to form solution C (purple),and C solution was aged in room temperature overnight to obtain purple precipitation. Then purple precipitation was washed and collected by centrifugal separation. In the end, the purple precipitation was calcined at 1073K for 300 min to obtain the ultimate product.

Characterization and measurements : Scanning electron microscopy (SEM) images and energy dispersive x-ray spectra were acquired on a Philips XL30 electron microscope (the Netherlands) operating at 20 kV. Transmission electron microscopy (TEM) images were taken with a JEOL2011 microscope (Japan) operating at 200 kV. Powder X-ray diffraction patterns were recorded on a

Bruker D4 X-ray diffractometer with Ni-filtered Cu Kαradiation (40 kV, 40 mA). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (SBET) using adsorption data in a relative pressure range from 0.011 to 0.98. By using the Density Functional Theory (DFT) method, the pore volumes and pore size distributions were derived from the desorption branches of the isotherms. The Raman spectra were recorded at room temperature on a LabRam-1B Raman spectrometer with a laser atan excitation wavelength of 632.8 nm.

Preparation of protein digestion： 1 mg of chicken egg ovalbumin (OVA) was dissolved 500 μL deionized water, and then the solution was boiled for 5 minutes make the protein degeneration. Then 500 μL 50 mM ammonium bicarbonate buffer at pH 8.0 was added in the solution. Next, the PNGase F (10U) was added into 100 μL mixed solution which has been denatured and then incubated at 37℃ overnight.

The zymolytic process of mouse brain tissue homogenate extracts is almost as same as the above. However, before incubated, mouse brain tissue homogenate extracts were centrifuged at 12000r for 10 min, the acquired supernatant (50 μL) was mingled with ammonium bicarbonate (25 mM, pH 8.0, 450 μL) and denatured .Then the endogenous peptides were removed by using ultrafiltration membrane at 14,000 g for 20 min.The obtained deposition were washed by ammonium bicarbonate (400 μL) for three times, and added into ammonium bicarbonate (25 mM, pH 8.0, 500 μL).

Protocol of enrichment process：Co-ZIF-67 materials (10 mg/ml, 50 μL) were added into a certain concentration of sample solution (such as OVA digestion,maltoheptaose and mouse brain tissue homogenate extracts) .After incubated for 30 min, the supernatant and materials were separated with magnetic separation, then the materials were washed with deionized water (100 μL) for 3 times. Finally, 5 μL 50% ACN was chose as eluent for MALDI-TOF-MS analysis.

MALDI-TOF MS analysis：1μL of Sample solution and DHB matrix solution (10 mg/mL, 0.1% TFA in 20% ACN/H_2O solution) were respectively spotted onto the MALDI plate in order, and then dried naturally.

positive ion mode on a 5800 Proteomics Analyzer (Applied Biosystems, USA) in the reflector

TOF detection modes was employed to detect the sample which was motivated by a Nd:YAG laser (383 nm) that was performed at a frequency of 200 Hz and accelerated voltage of 20 kV.

Search parameters : The detailed structures of N-linked glycans were searched from Glycoworkbench and mass tolerances of the glycan structure was 1 Da.

Scheme S1 Schematic illustration of the procedure for size-selective enrichment of glycans by Co-ZIF-67 materials.

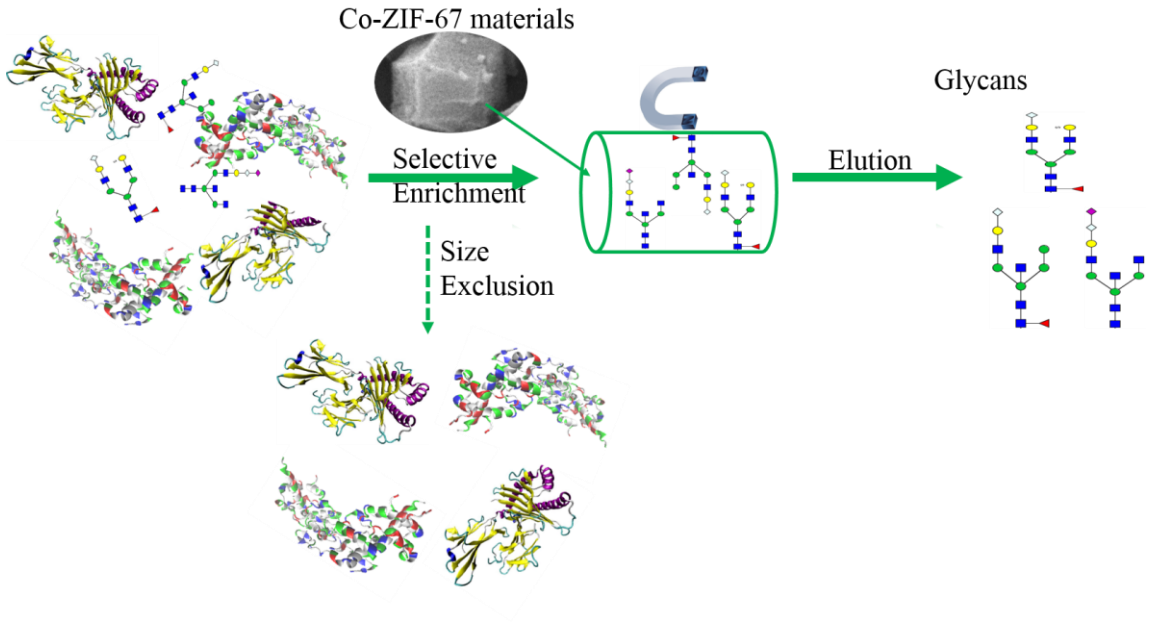


Fig. S1. Co-ZIF-67 materials dispersed in water and magnetically separated.

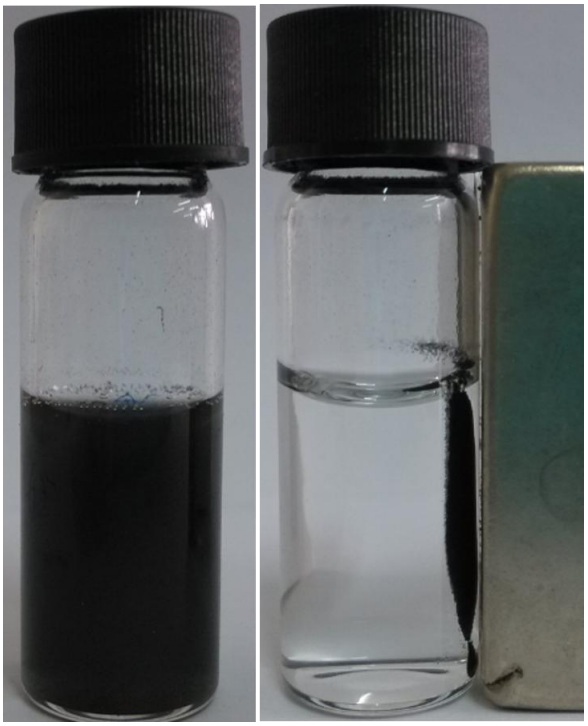


Fig. S2. Chemical structure of ZIF-67 crystals. Ball-and-stick representation of the second building units showing the coordination environment around cobalt (a). Packing diagram of ZIF-67 crystals (b). Hydrogen atoms are omitted for clarity. Co light purple, C black, N blue.

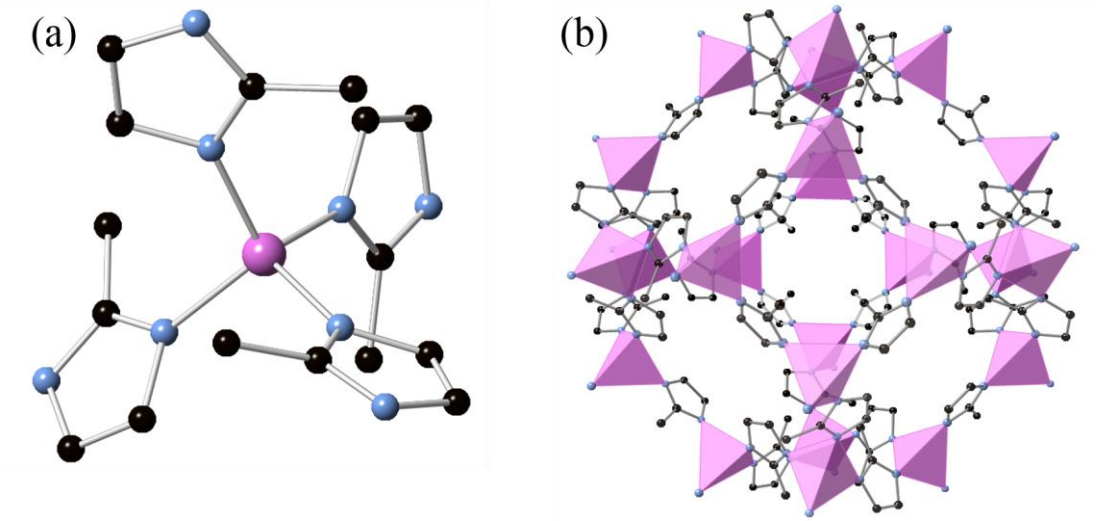


Fig. S3. XRD patterns of (a) ZIF-67crystals and (b) Co-ZIF-67 materials.

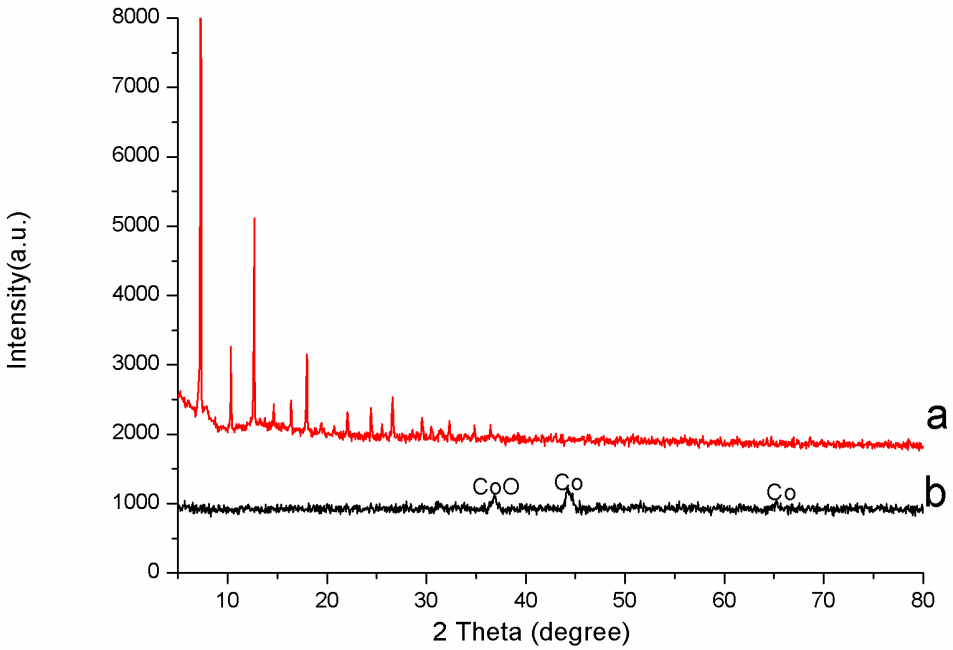


Fig. S4. The energy dispersive X-ray (EDX) spectrum of (a) ZIF-67 crystals and (b) Co-ZIF-67 materials.

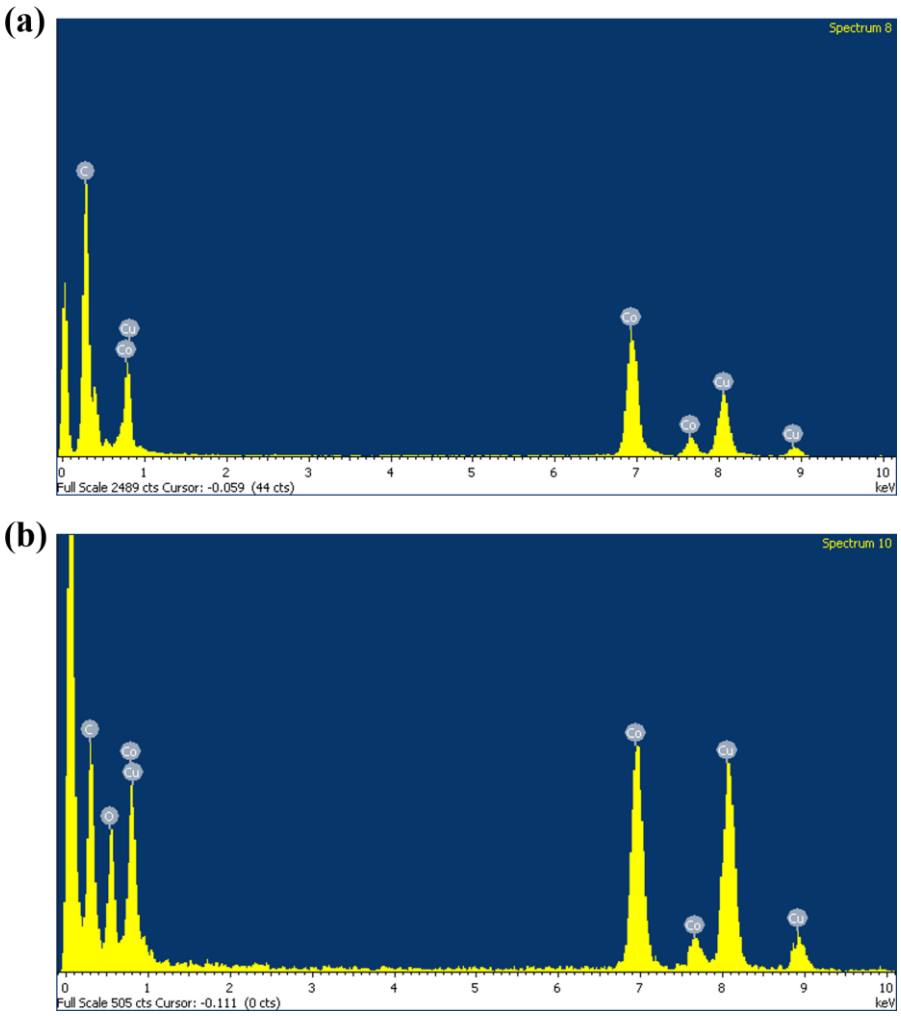


Fig. S5. SEM (a) and TEM (b) images of ZIF-67crystals.

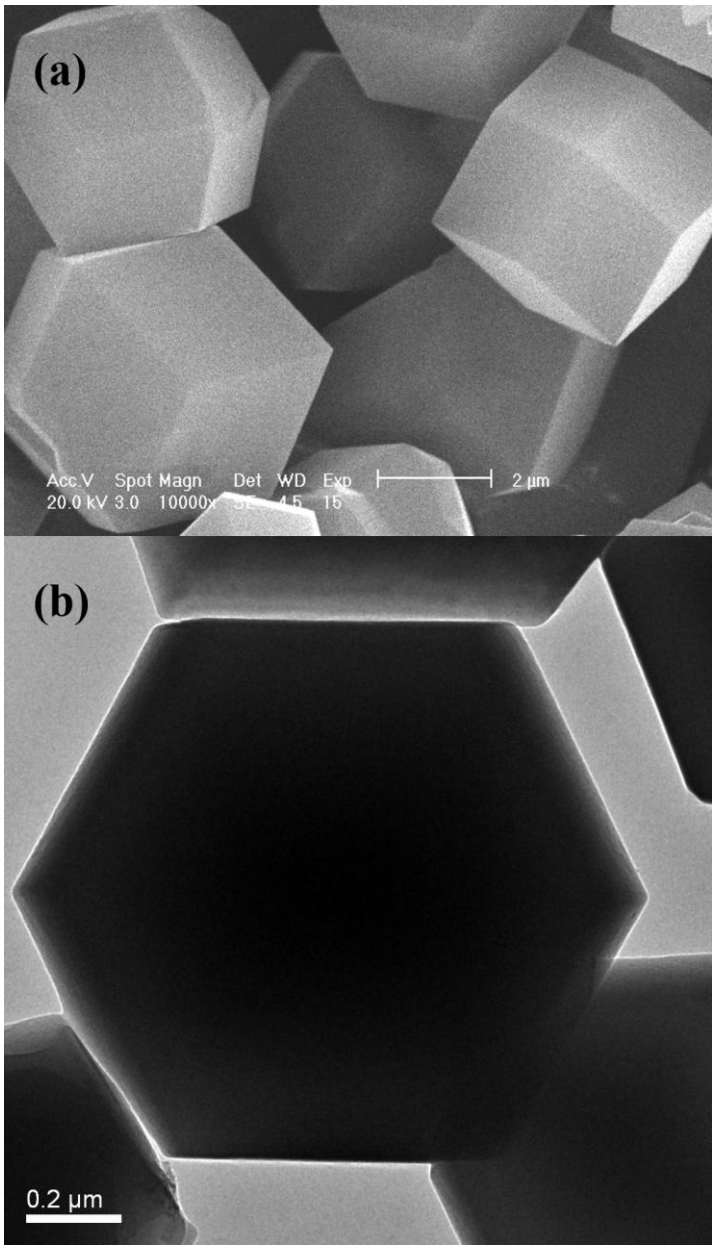


Fig. S6. Raman spectrum of Co-ZIF-67 materials.

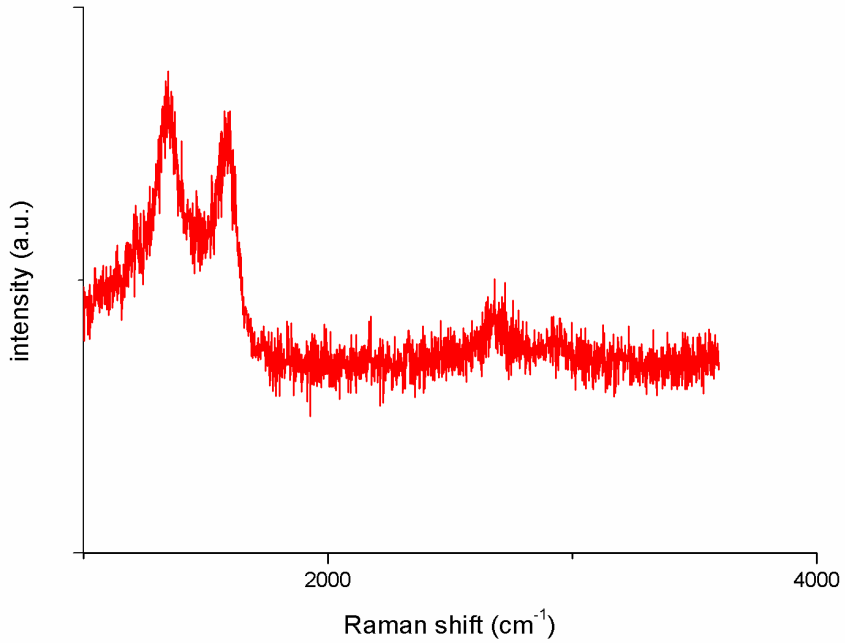


Fig. S7. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of Co-ZIF-67 materials.

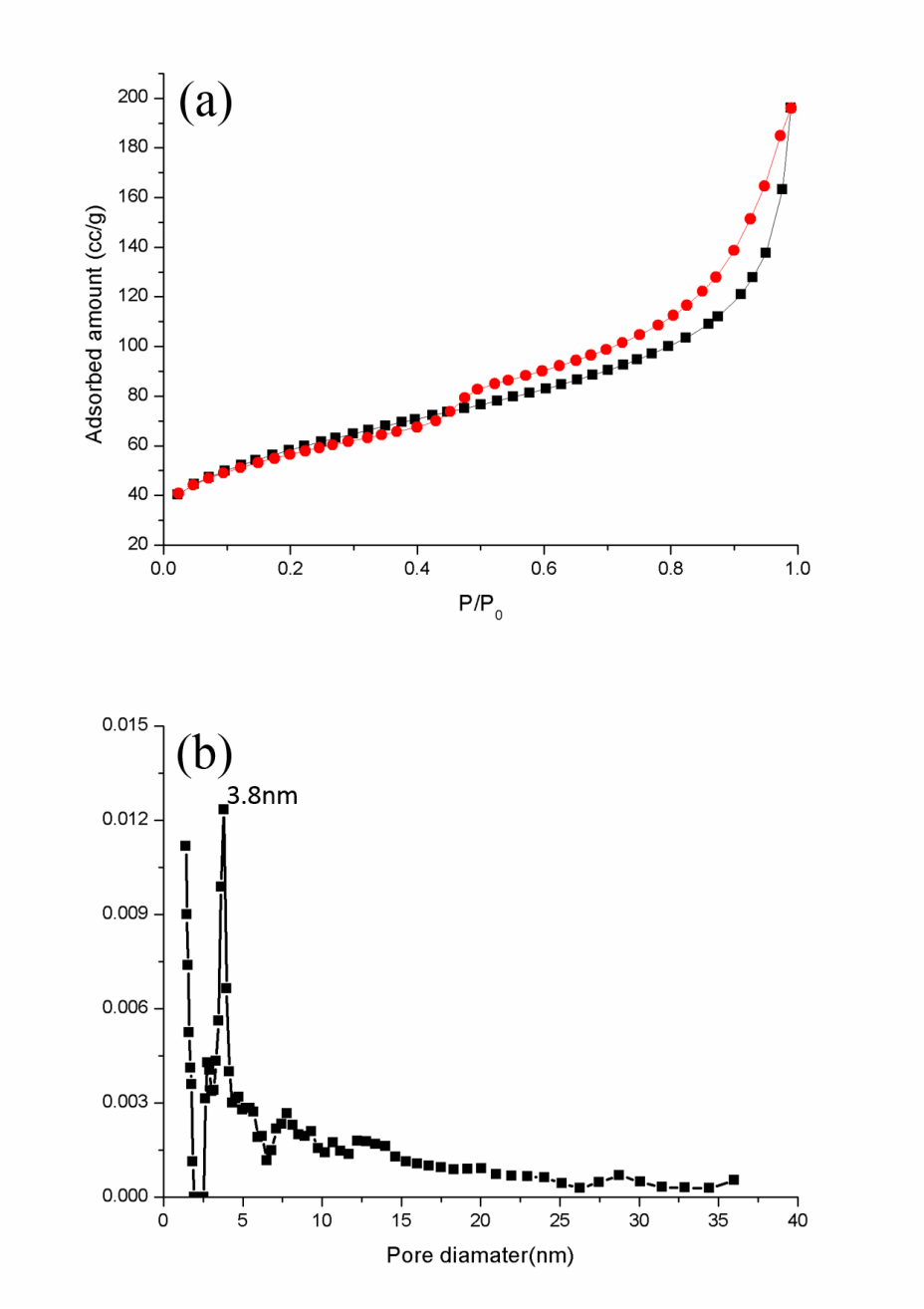


Fig.S8. MALDI-TOF MS for N-linked glycan enriched by using carbon-functionalized graphene/mesoporous silica materials from ovalbumin digests with different concentration: (a)25 ng/μL; (b) 5 ng/μL.

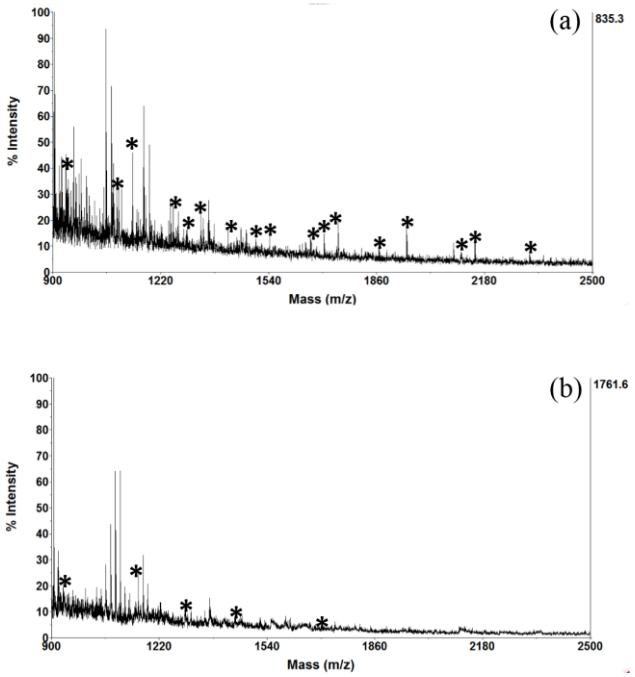


Fig.S9. MALDI-TOF MS analysis of N-linked glycans before Co-ZIF-67 materials enrichment from ovalbumin digests containing BSA and ovalbumin with different ratio (W/W). The ratio of ovalbumin digests/ovalbumin/BSA was 1:50:50 (a), 1:100:100 (b) and 1:300:300(c), respectively. The mark "*" in mass spectra image denotes glycans which was released from ovalbumin. The up-right insets were spectra detected interferential protein.

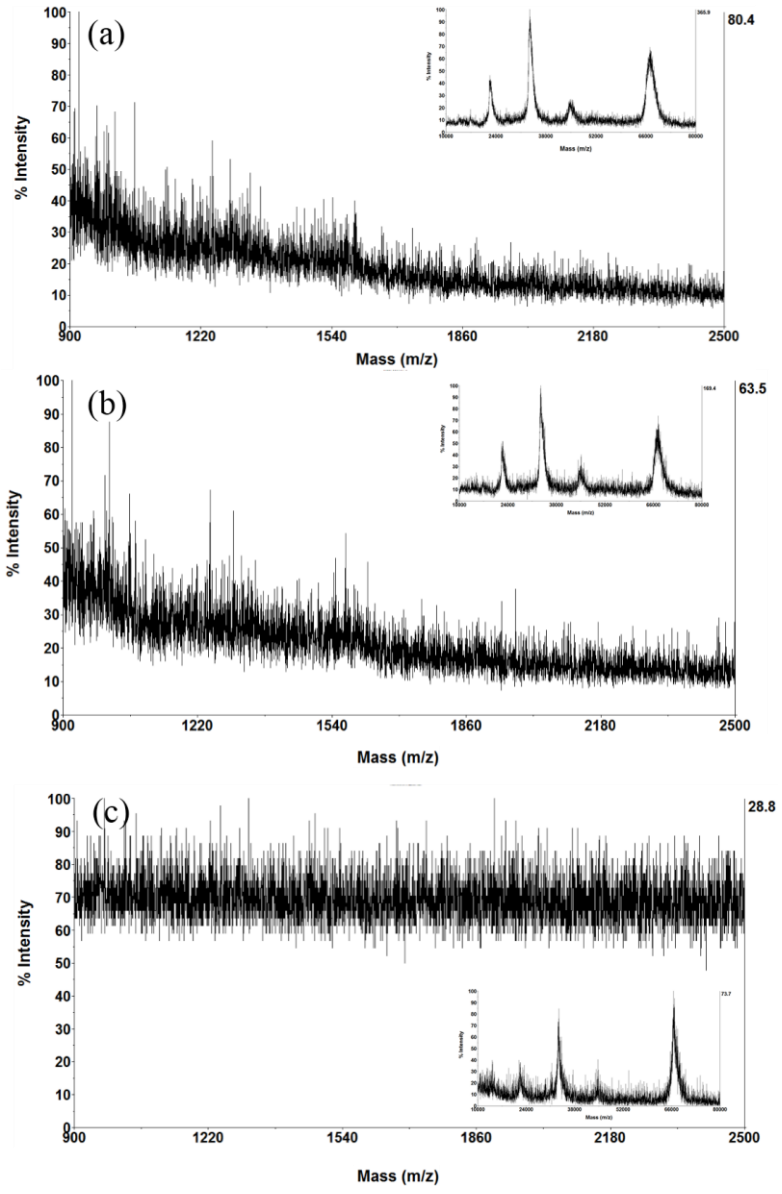


Fig. S10 . MALDI-TOF MS analysis of N-linked glycans after active carbon enrichment from ovalbumin digests containing BSA and ovalbumin with different ratio (W/W). The ratio of ovalbumin digests/ ovalbumin/ BSA was 1:50:50 (a), 1:100:100 (b) and 1:300:300(c), respectively. The mark "*" in mass spectra image de-notes glycans which was released from ovalbumin.

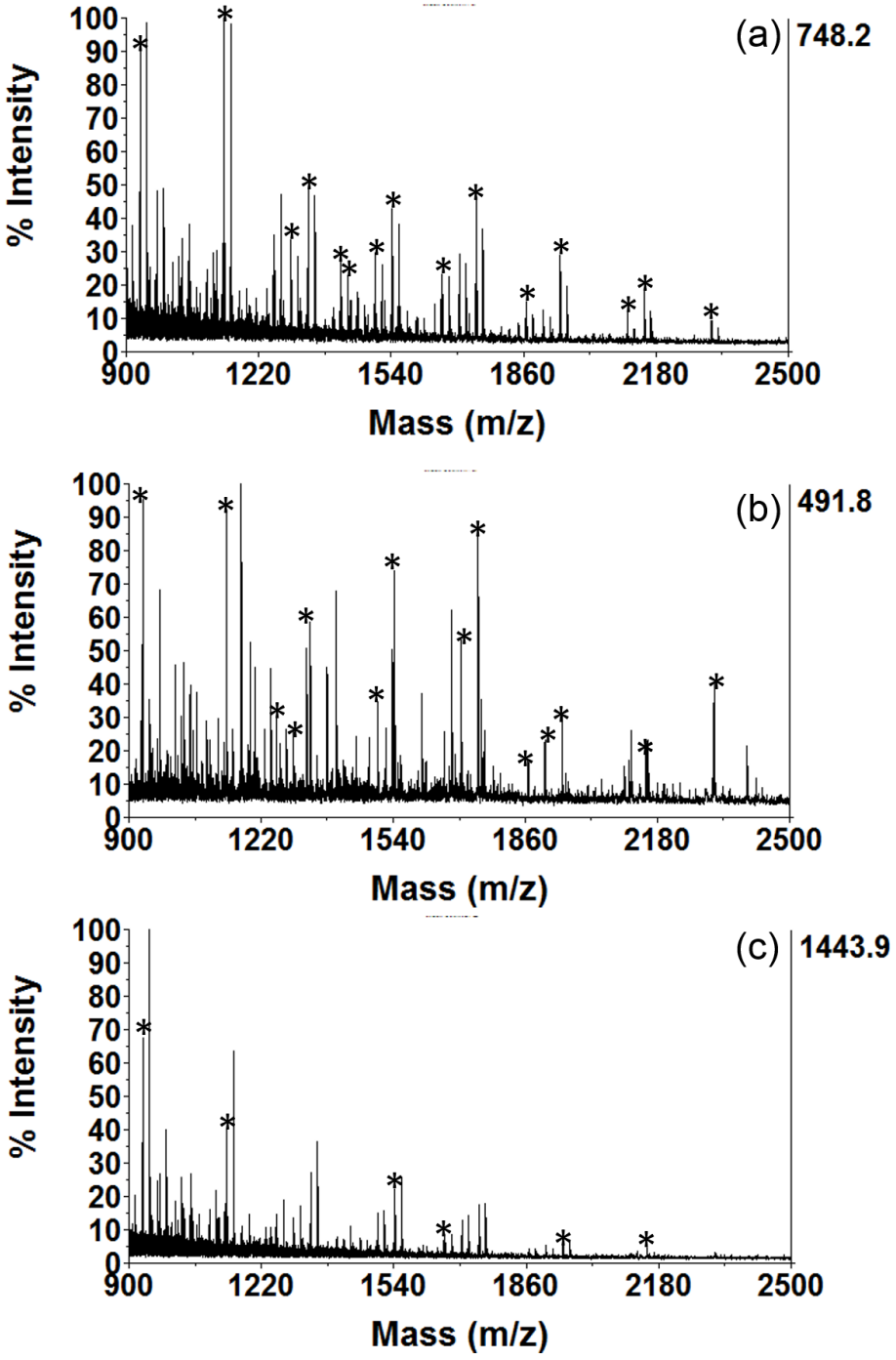


Fig. S11. MALDI mass spectrum of N-linked glycans enriched from ovalbumin using Co-ZIF-67 materials,(a)for the first time and (b)for the third time,where the "*" indicates the N-linked glycans and "#" indicates the maltoheptaose (internal standard).

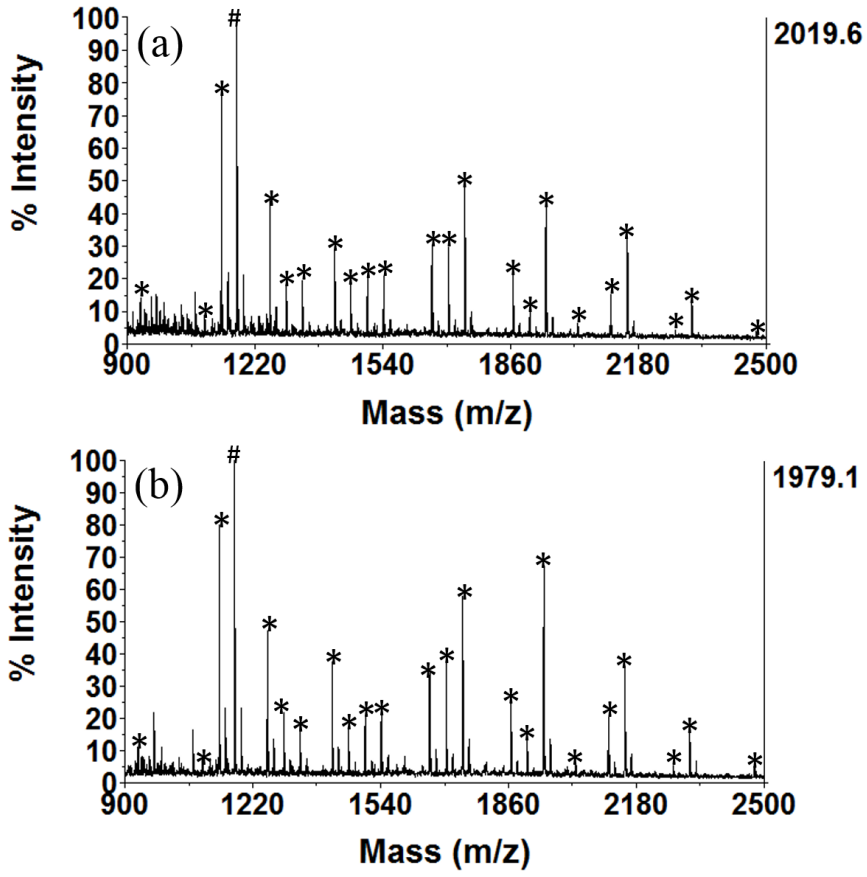
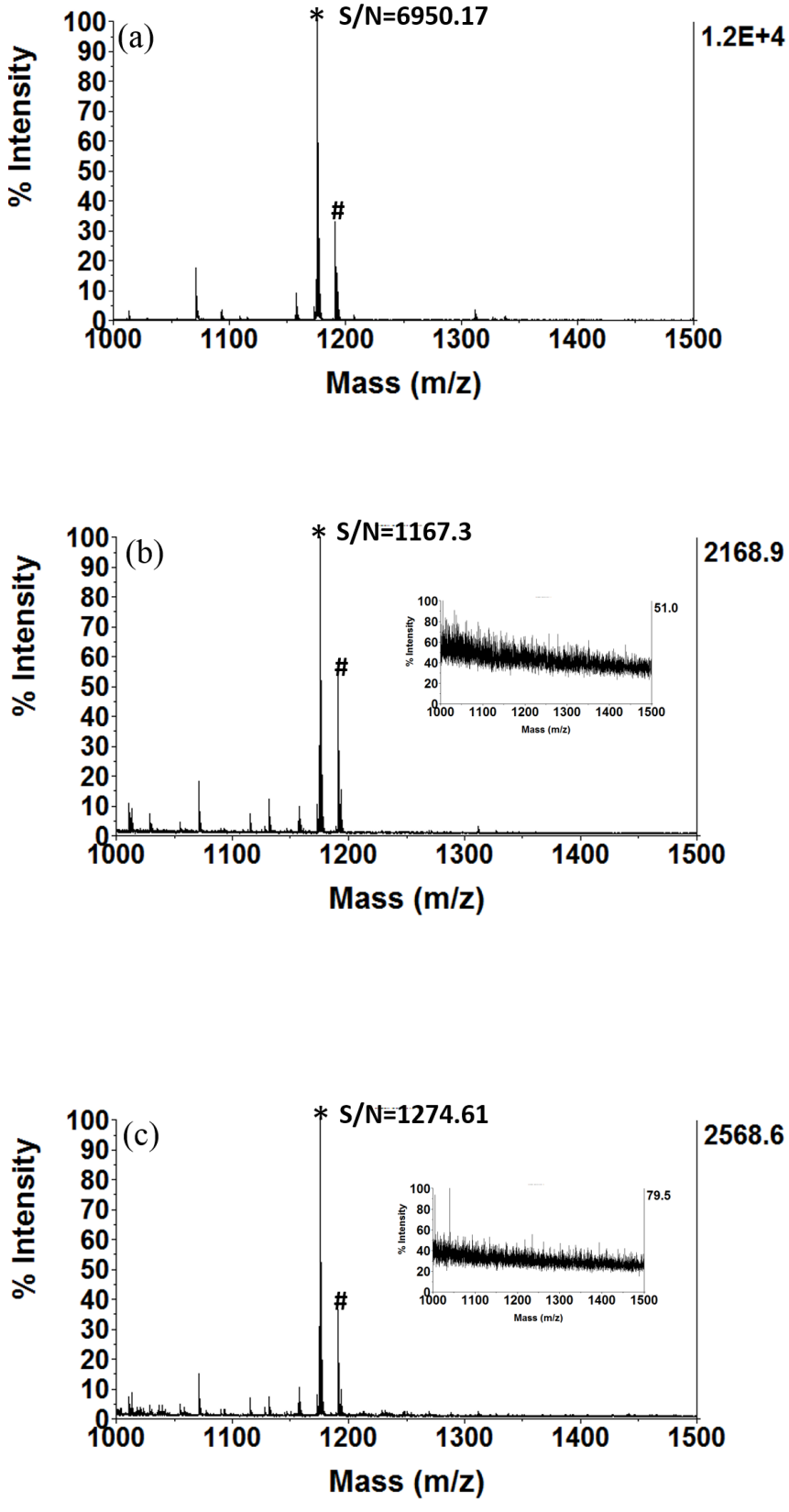
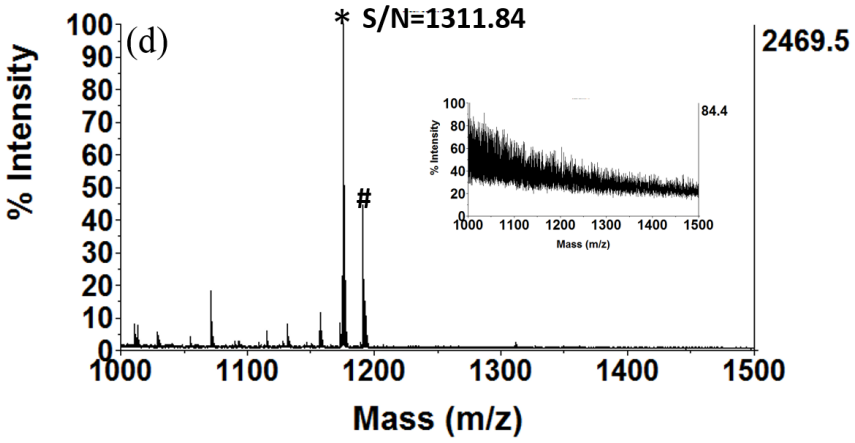
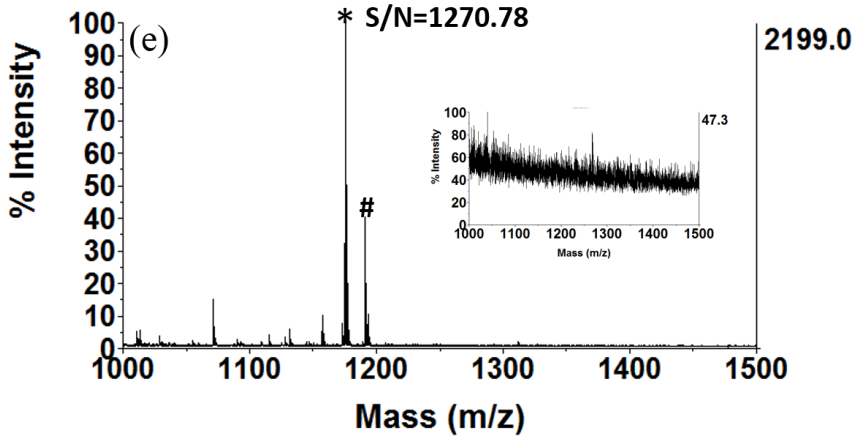
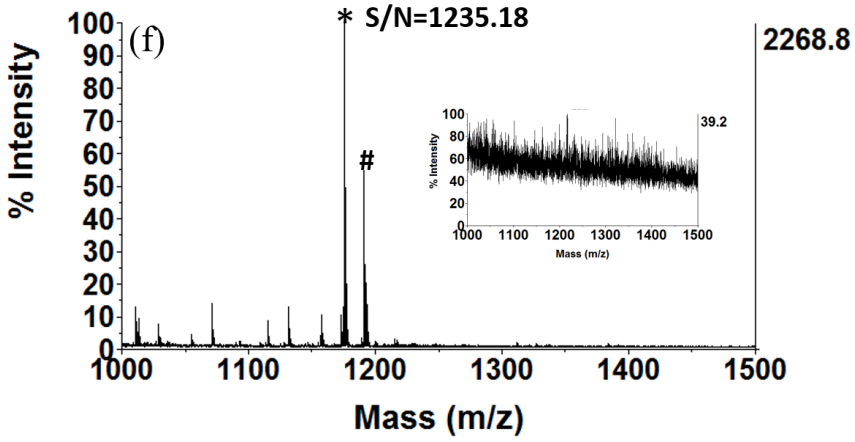


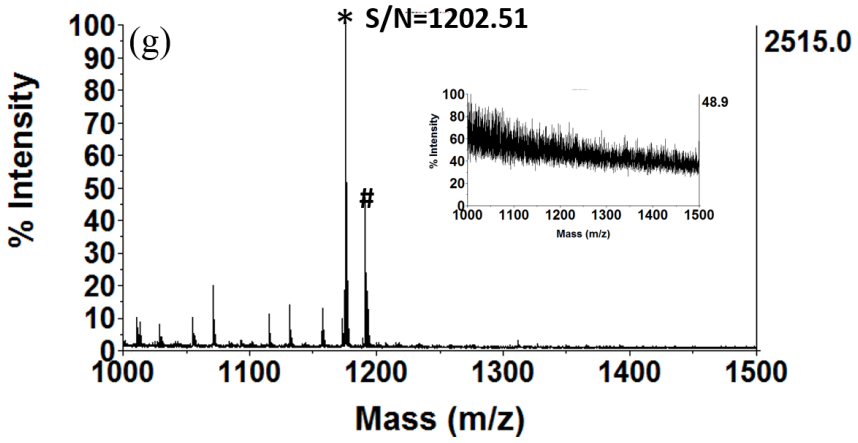
Fig. S12. Mass spctrum of (a) 500 ng maltoheptaose and (b-i) the elution (5μL, 1μL was spotted on the MALDI plate) after enrichment with Co-ZIF-67 materials. (Insert, supernatant after enrichment with Co-ZIF-67 materials.)

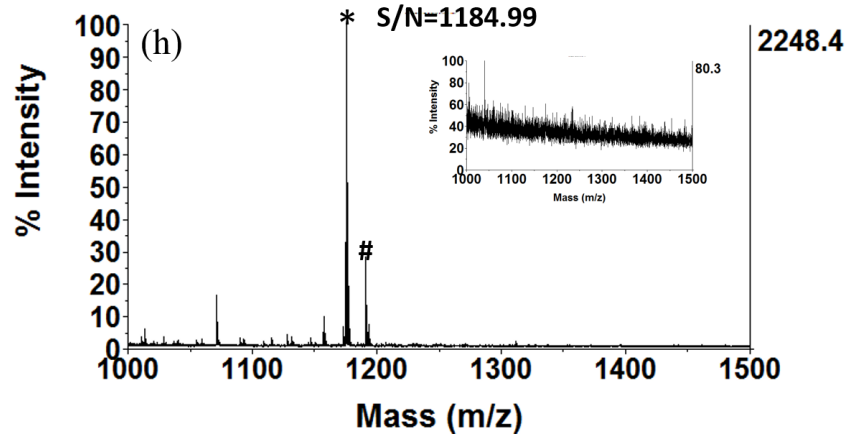



(d)
* S/N=1311.84
2469.5
84.4
#
% Intensity
Mass (m/z)


(e)
* S/N=1270.78
2199.0
47.3
#
% Intensity
Mass (m/z)


(f)
* S/N=1235.18
2268.8
39.2
#
% Intensity
Mass (m/z)


(g)
* S/N=1202.51
2515.0
48.9
#
% Intensity
Mass (m/z)


(h)
* S/N=1184.99
2248.4
80.3
#
% Intensity
Mass (m/z)

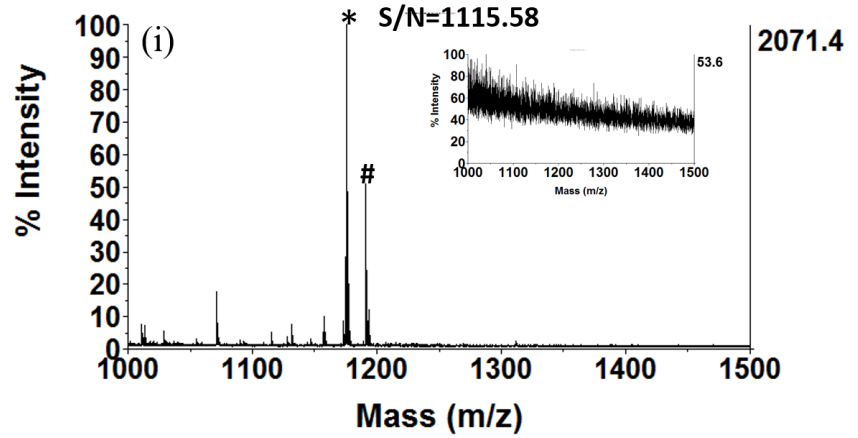

(i)
* S/N=1115.58
2071.4
53.6
#
% Intensity
Mass (m/z)

Fig. S13. MALDI-TOF mass spectra of N-linked glycans in human serum digestion (a) without enrichment and (b) after enrichment with Co-ZIF-67 materials.

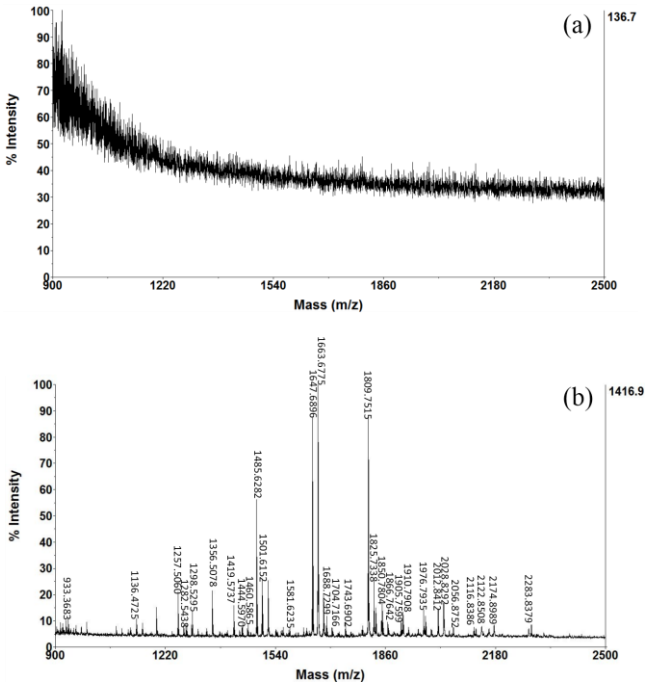


Fig. S14. MALDI-TOF mass spectra of N-linked glycans in mouse brain tissue digestion (a) without enrichment and (b) after enrichment with Co-ZIF-67 materials.

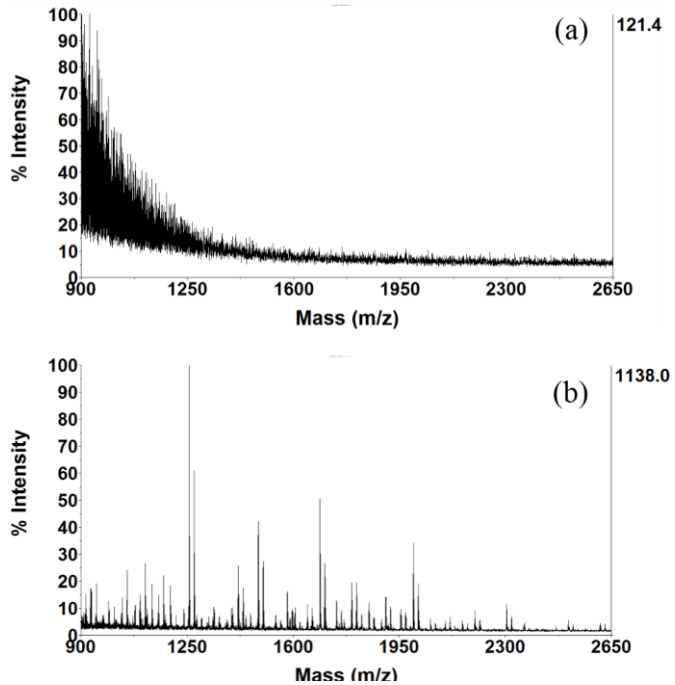
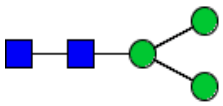
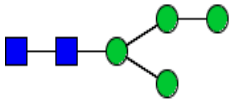
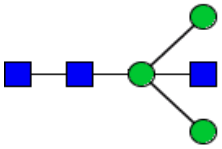
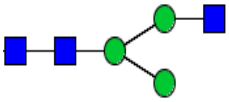
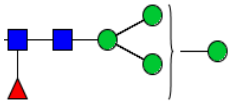
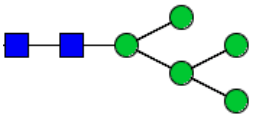
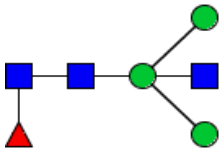
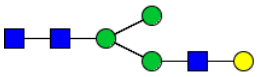
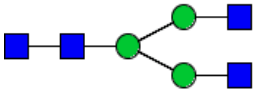
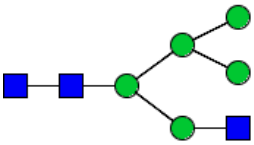
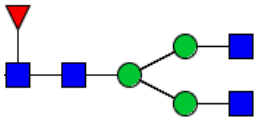
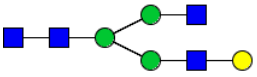
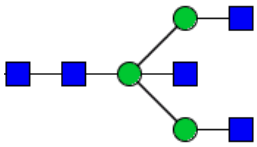
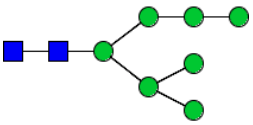
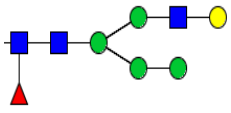
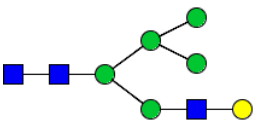


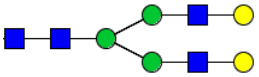
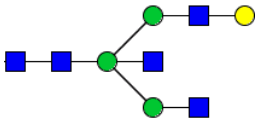
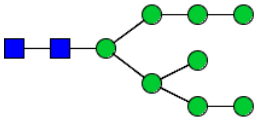
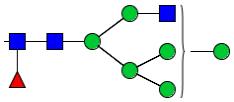
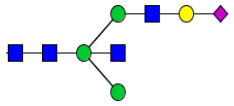
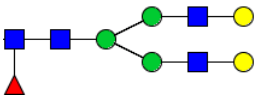
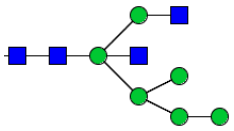
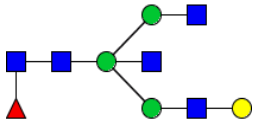
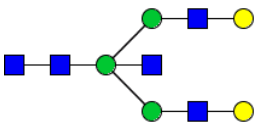
Table S1. The S/N ratios of 500 ng maltoheptaose and the elution(5 μL,1 μL was spotted on the the MALDI plate) after enrichment with Co-ZIF-67 materials and calculated recovery of the maltoheptaose on Co-ZIF-67 materials.

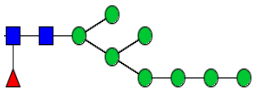
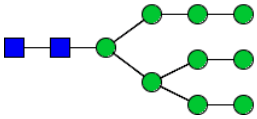
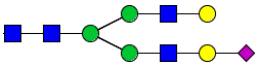
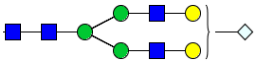
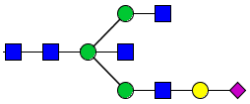
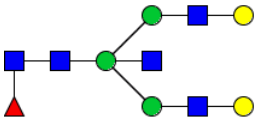
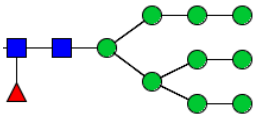
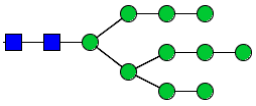
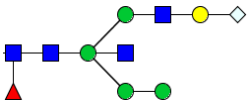
No.	S/N	Recovery (%)
1	1167.3	83.98
2	1274.61	91.69
3	1311.84	94.37
4	1270.78	91.42
5	1235.18	88.86
6	1202.51	86.51
7	1184.99	85.25
8	1115.58	80.26
500 ng maltoheptaose (S/N = 6950.17)		

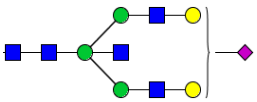
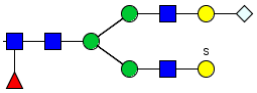
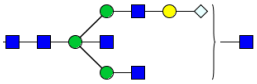
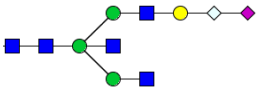
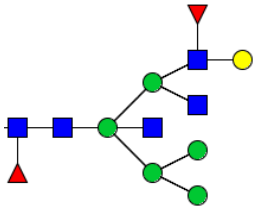
Table S2. The detected forty of N-glycans from mouse brain tissue by enriching with Co-ZIF-67 materials (N-linked glycans were released by PNGase F digestion, and glycan strcutures were searched from Glycoworkbench through the Mol. wt of oligosaccharide. Part of the strcutures has been demonstrated. ●, Mannose; ○, Galactose; ■, GlcNAc; ◆, Sialic Acid; ▲, Fucose; ◇, N-glycolyl sialic acid.)

No	M/Z ($[M+nNa]^+$)	Structure (M)
1	933.2	
2	1095.3	
3	1136.3	
4	1217.3	
5	1241.4	
6	1256.4	
7	1282.4	

8	1298.4	
9	1339.4	
10	1460.2	
11	1485.5	
12	1501.4	
13	1541.5	
14	1581.4	
15	1606.5	
16	1622.5	

17	1663.5	
18	1704.5	
19	1743.2	
20	1768.5	
21	1792.5	
22	1809.5	
23	1825.5	
24	1850.6	
25	1866.5	

26	1890.6	
27	1905.2	
28	1954.6	
29	1970.6	
30	1995.6	
31	2012.6	
32	2052.6	
33	2068.6	
34	2116.6	

35	2157.6	
36	2198.7	
37	2214.6	
38	2303.7	
39	2319.6	
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