

Supporting Information

Zr-based metal–organic frameworks for specific and size-selective enrichment of phosphopeptides with simultaneous exclusion of proteins

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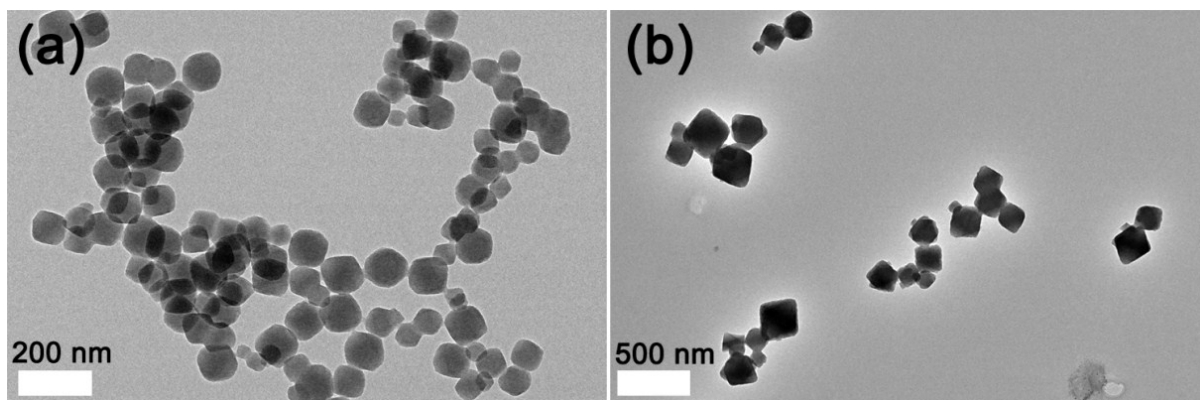


Fig. S1 TEM images of the as-synthesized (a) UiO-66 and (b) UiO-67 nanoparticles (NPs).

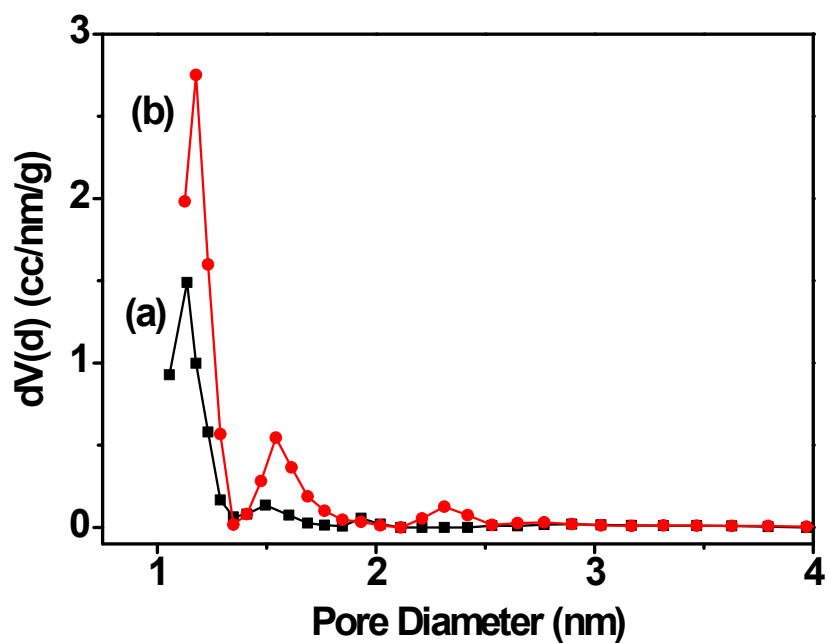


Fig. S2 DFT pore size distribution of the as-synthesized (a) UiO-66 and (b) UiO-67 NPs.

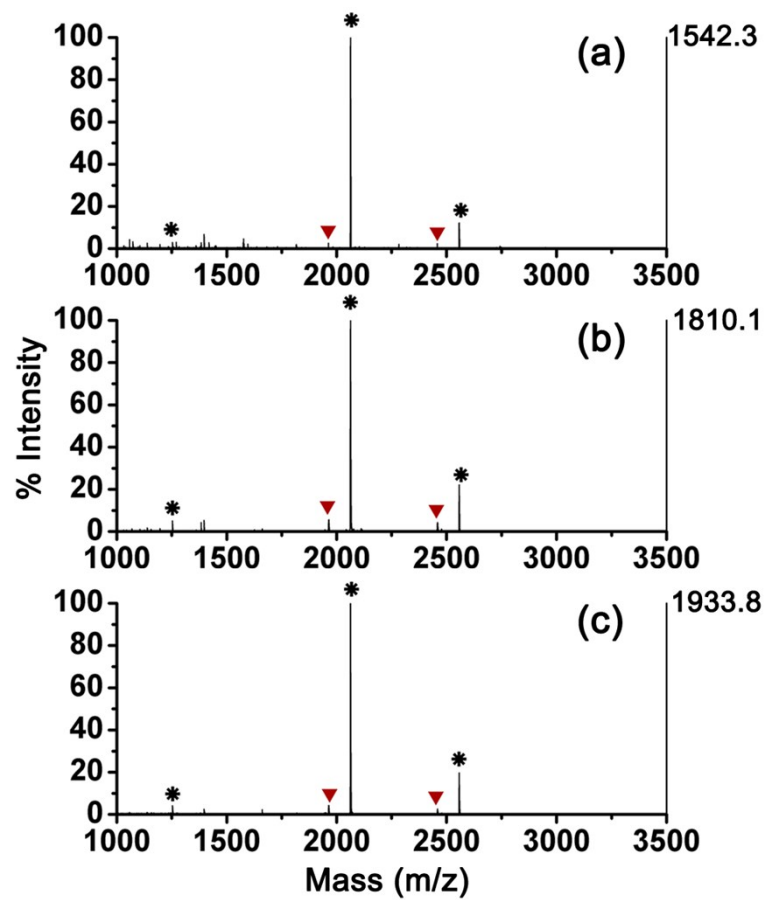


Fig. S3 MALDI-TOF mass spectra for the peptides derived from β -casein tryptic digest enriched by UiO-67 NPs using the loading buffer containing (a) 0.5%, (b) 1% and (c) 2% TFA.

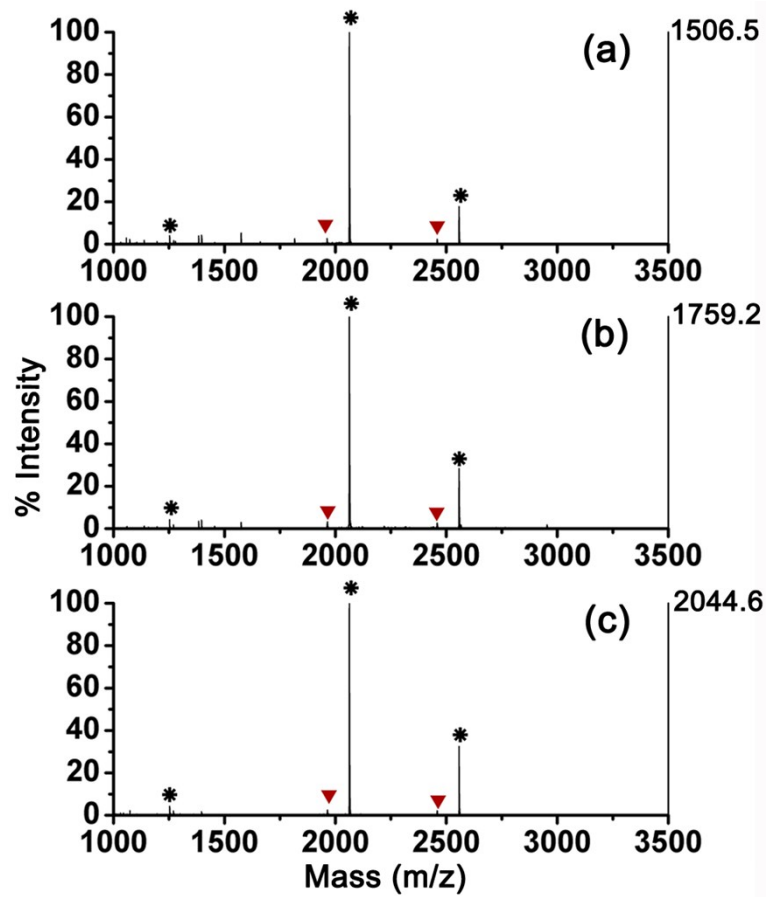


Fig. S4 MALDI-TOF mass spectra for the peptides derived from β -casein tryptic digest enriched by UiO-67 NPs using the loading buffer containing (a) 10%, (b) 30% and (c) 50% ACN.

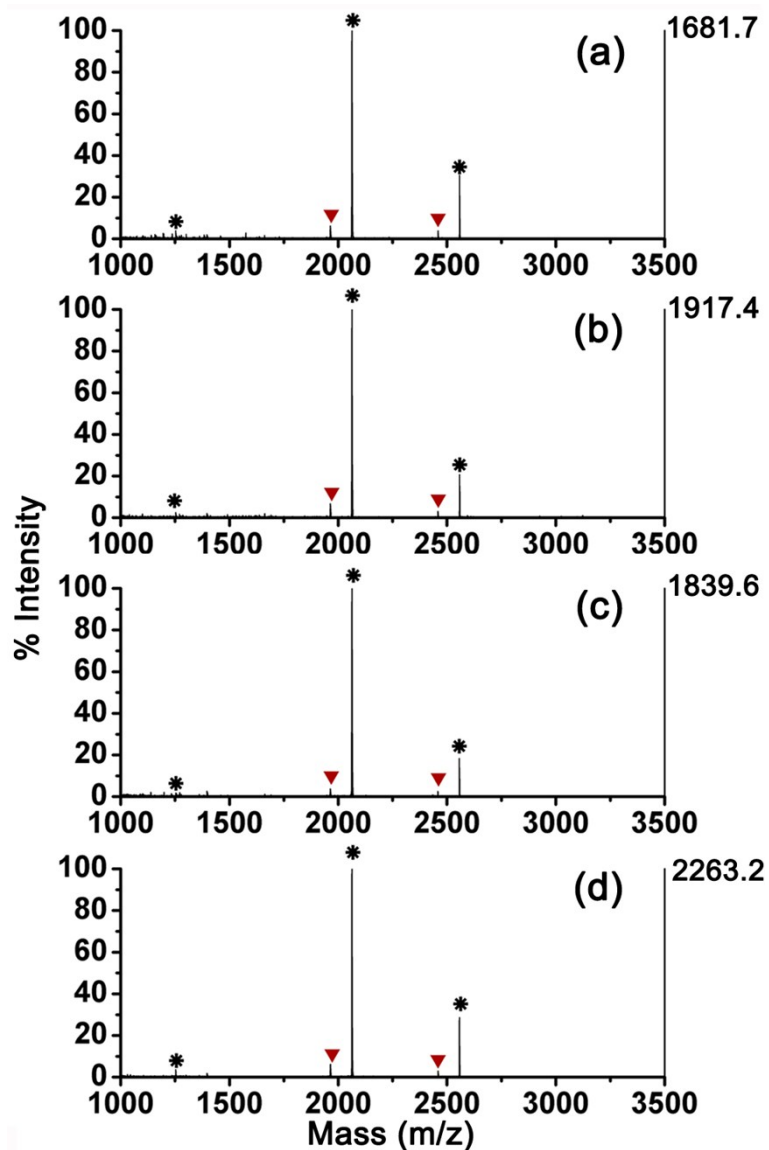


Fig. S5 MALDI-TOF mass spectra for the peptides derived from β -casein tryptic digest after enrichment with UiO-67 NPs using different washing protocols: (a) rinsed with 10% ACN/0.1% TFA for three times, (b) rinsed with 30% ACN/0.1% TFA for three times, (c) rinsed with 50% ACN/0.1% TFA for three times and (d) rinsed with 30% ACN/0.1% TFA containing 200 mM NaCl for once and subsequently washed with 30% ACN/0.1% TFA for twice.

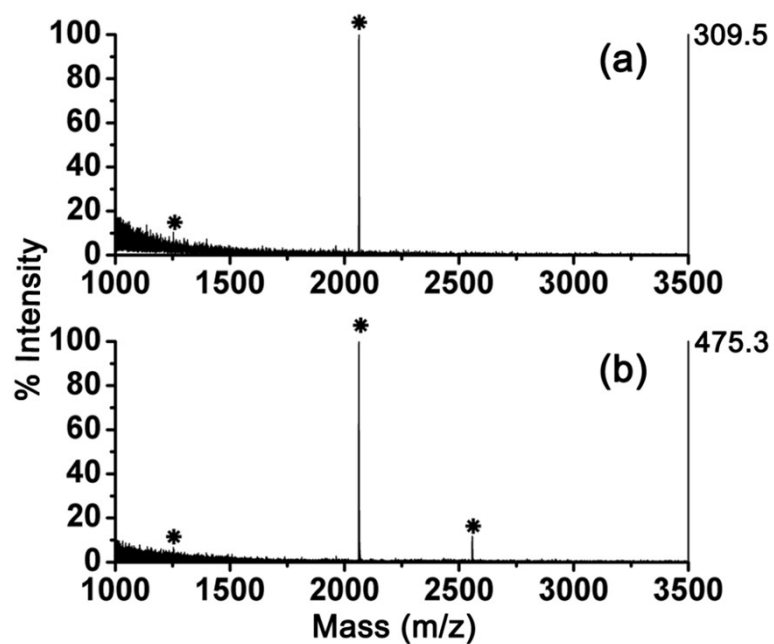


Fig. S6 MALDI-TOF mass spectra of 0.1 fmol μL^{-1} β -casein tryptic digest after enrichment by (a) UiO-66 and (b) UiO-67 NPs using the optimized protocol.

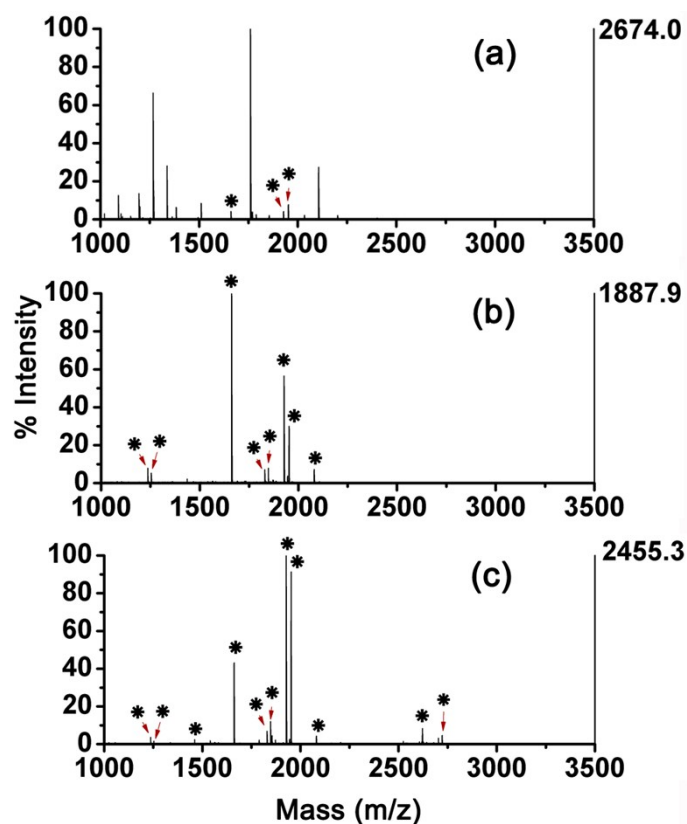


Fig. S7 MALDI-TOF mass spectra of digest of α -casein (5 pmol) by (a) direct analysis, and enrichment with (b) UiO-66 and (c) UiO-67 NPs. \nearrow indicates phosphopeptides.

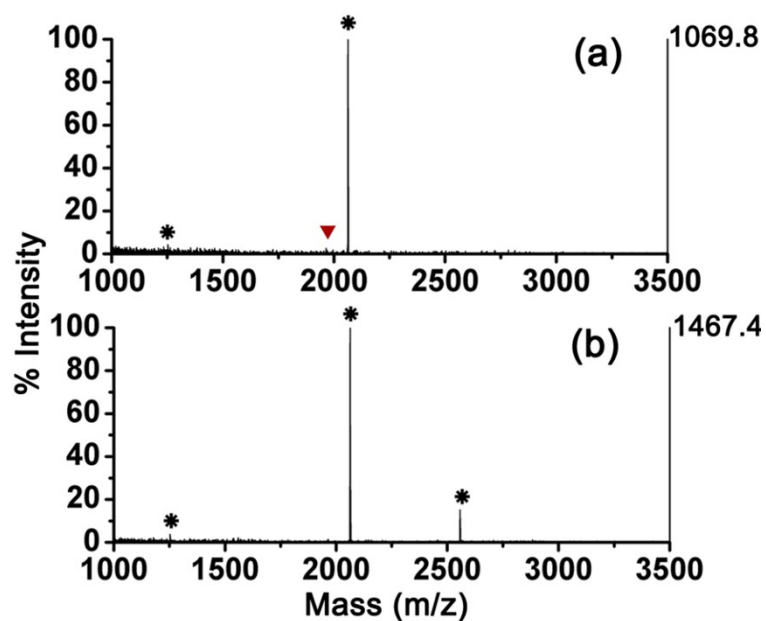


Fig. S8 MALDI-TOF mass spectra of peptide mixtures of tryptic digests of β -casein and BSA with molar ratio of 1:200 after enrichment by (a) UiO-66 and (b) UiO-67 NPs.

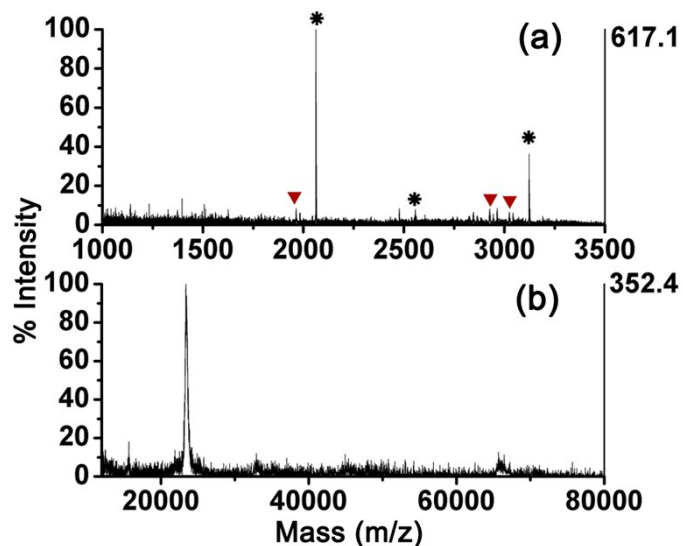


Fig. S9 MALDI-TOF mass spectra of tryptic digests of β -casein, undigested α -casein and BSA with molar ratio of 1:100:100 enriched by commercially available ZrO_2 : (a) peptides analysis and (b) proteins analysis. $\square \nearrow$ and \odot indicate phosphopeptides and their dephosphorylated counterparts, respectively.

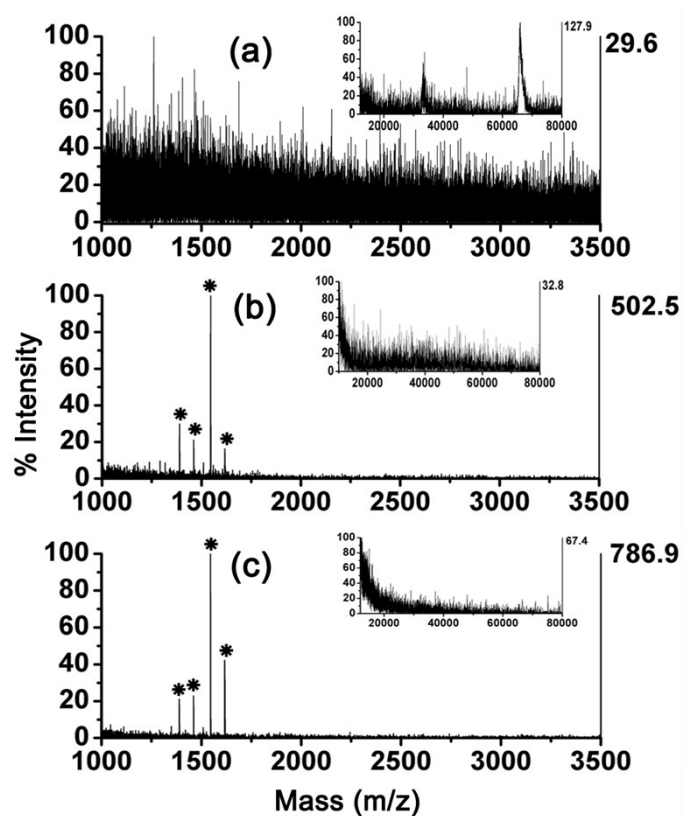


Fig. S10 MALDI-TOF mass spectra of human serum by (a) direct analysis, and enrichment with (b) UiO-66 and (c) UiO-67 NPs. $\square \nearrow$ indicates phosphopeptides.

Table S1. Phosphopeptides identified from human serum after enrichment with UiO-66 and UiO-67

Peak no	m/z	peptide sequence
1	1389	D[pS]GEGDFLAEGGGV
2	1460	AD[pS]GEGDFLAEGGGV
3	1545	D[pS]GEGDFLAEGGGVR
4	1616	AD[pS]GEGDFLAEGGGVR