

## Supporting Information

### Poly(guanidinium ionic liquid)s Particles as Affinity Platform for Highly Selective Enrichment of Phosphopeptides

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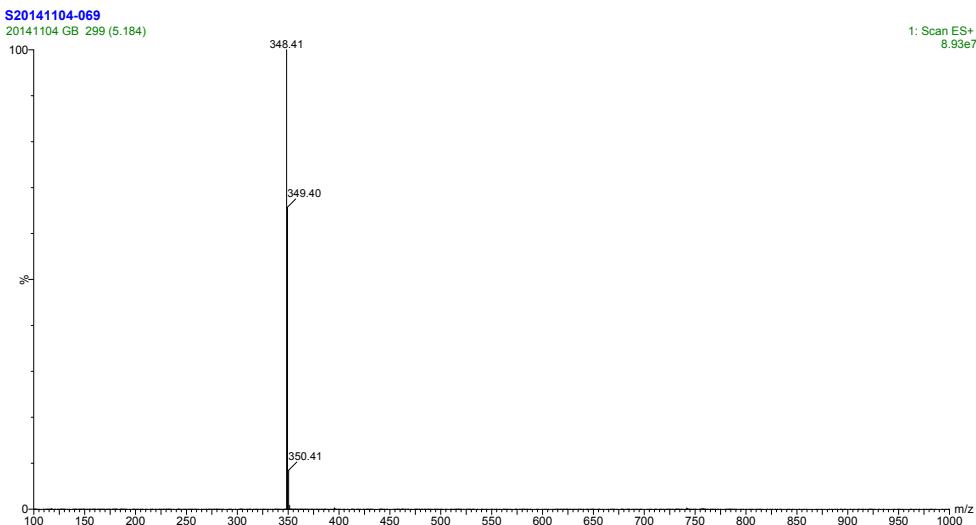


Figure S1. HPLC-MS spectroscopy of guanidine ionic liquids.

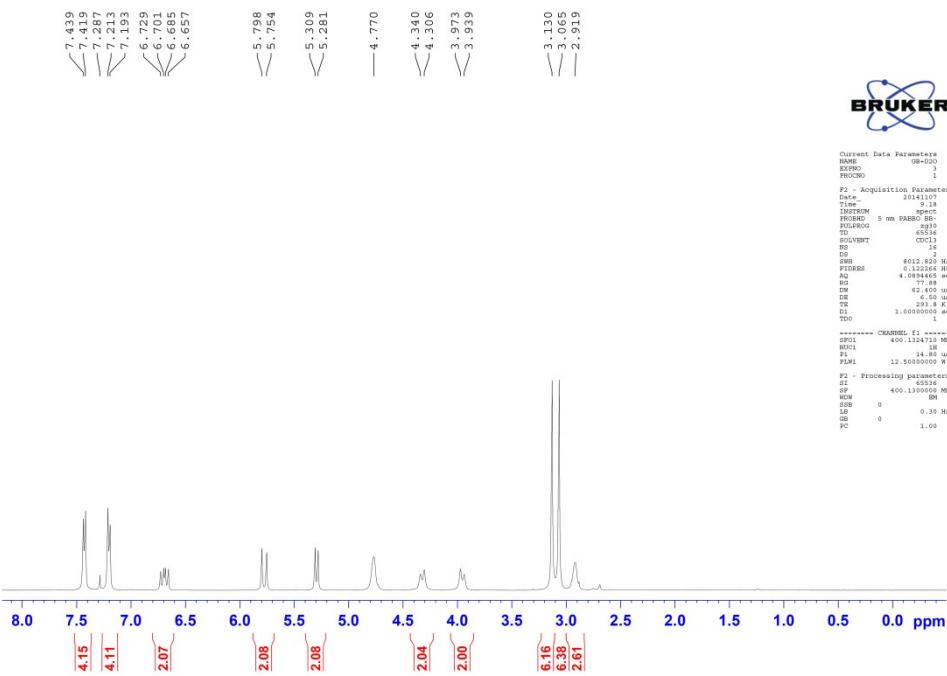


Figure S2  $^1\text{H}$  NMR spectra of guanidine ionic liquids

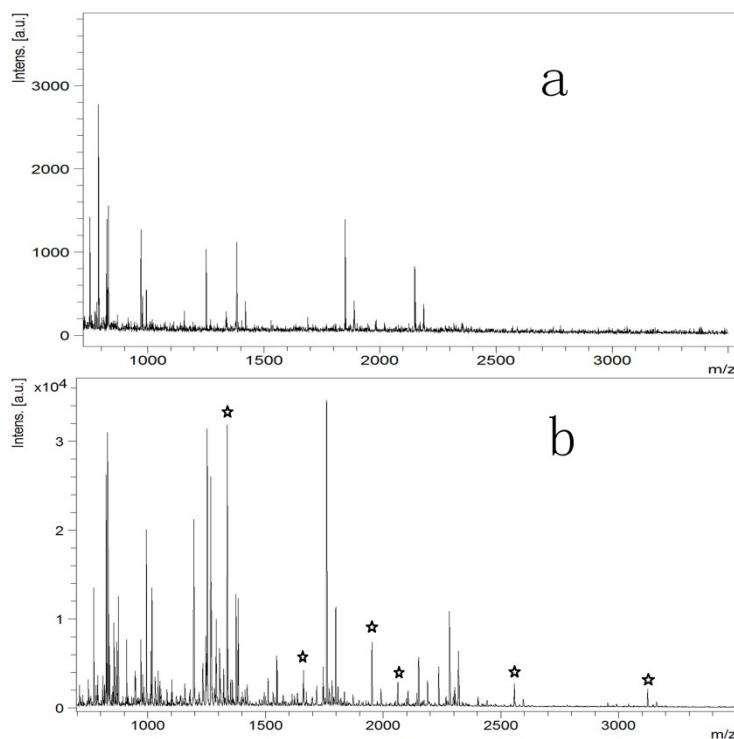


Figure S3 MALDI-TOF mass spectra for the peptides derived from the tryptic digest of the milk. Direct analysis (a), after enrichment (b). (★:phosphopeptides).

Table S1. List of phosphopeptides identified from tryptic digest of  $\beta$ -casein after enriched by poly (guanidyl ionic liquid)s in MALDI-TOF MS analysis.

NO.	Peptide sequence	Number of phosphoryl groups	Observed m/z
$\beta$ 1	FQ[pS]EEQQQTEDELQDK	1	2062.002
$\beta$ 2	FQ[pS]EEQQQTEDELQDKIHPF	1	2556.130
$\beta$ 3	RELEELNVPGEIVE[pS]L[pS][pS][pS]EESITR	1	3121.341

[pS]: phosphorylated site

Table S2. List of phosphopeptides identified from tryptic digest of nonfat milk after enriched by poly (guanidyl ionic liquid)s in MALDI-TOF MS analysis.

NO.	Peptide sequence	Number of phosphoryl groups	Observed m/z
1	TVDME[pS] TEVF	1	1237.392
2	TVD[Mo]ME[PS] TEVF	1	1252.429
3	HIQKEDV[pS]ER	1	1337.509
4	VPQLEIVPN[pS] AEER	1	1660.591
5	YKVPQLEIVPN[pS] AEER	1	1951.711
6	FQ[pS] EEQQQTEDELQDK	1	2061.568
7	FQ[pS] EEQQQTEDELQDKIHPF	1	2555.732
8	RELEELNVPGEIVE[pS]L[pS][pS]EESITR	1	3121.768

[pS]: phosphorylated site

Table S3. List of phosphopeptides identified from tryptic digest of milk after enriched by poly (guanidyl ionic liquid)s in MALDI-TOF MS analysis.

NO.	Peptide sequence	Number of phosphoryl groups	Observed m/z
1	HIQKEDV[pS]ER	1	1337.509
2	VPQLEIVPN[pS] AEER	1	1660.591
3	YKVPQLEIVPN[pS] AEER	1	1951.711
4	FQ[pS] EEQQQTEDELQDK	1	2061.568
5	FQ[pS] EEQQQTEDELQDKIHPF	1	2555.732
6	RELEELNVPGEIVE[pS]L[pS][pS]EESITR	4	3121.768

[pS]: phosphorylated site