

Electronic Supplementary Information

Mesoporous polymeric microspheres with high affinity for phosphorylated biomolecules.

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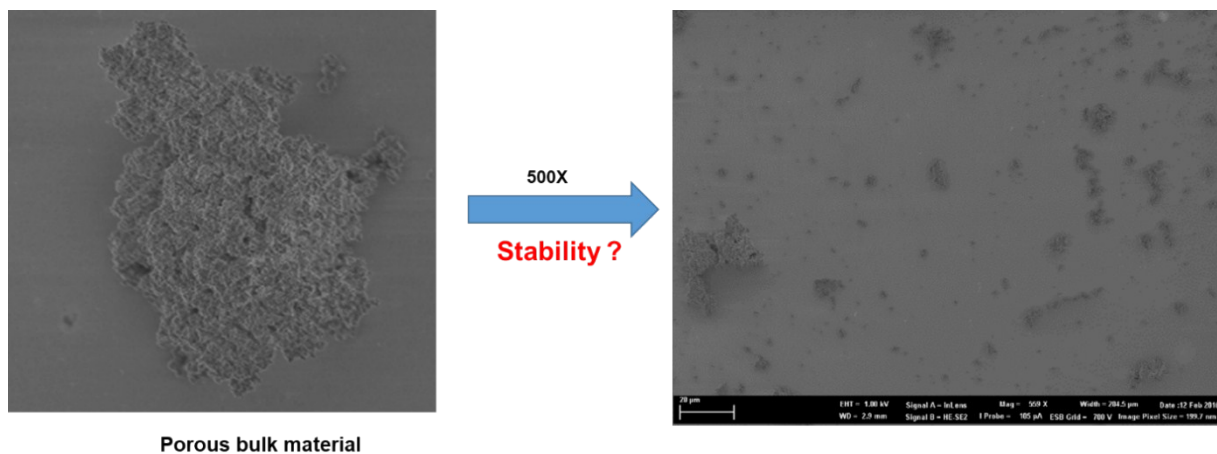


Figure S1. The SEM images of porous bulk monolith particles. The porous bulk monoliths (left side) was disintegrated into smaller particles (right side) after pressing with spatula or by normal hand press.

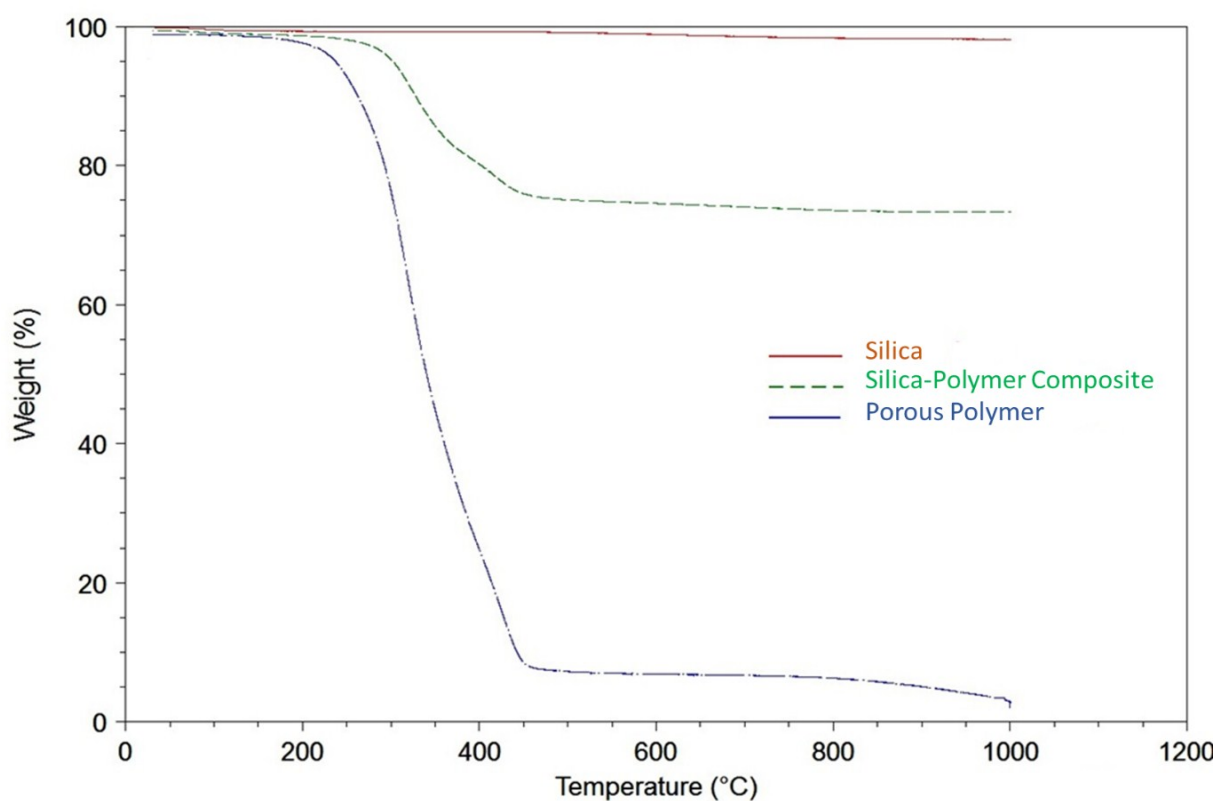


Figure S2. Thermal gravimetric analysis traces (TGA) graph of porous silica, silica-polymer composite and porous polymer respectively.

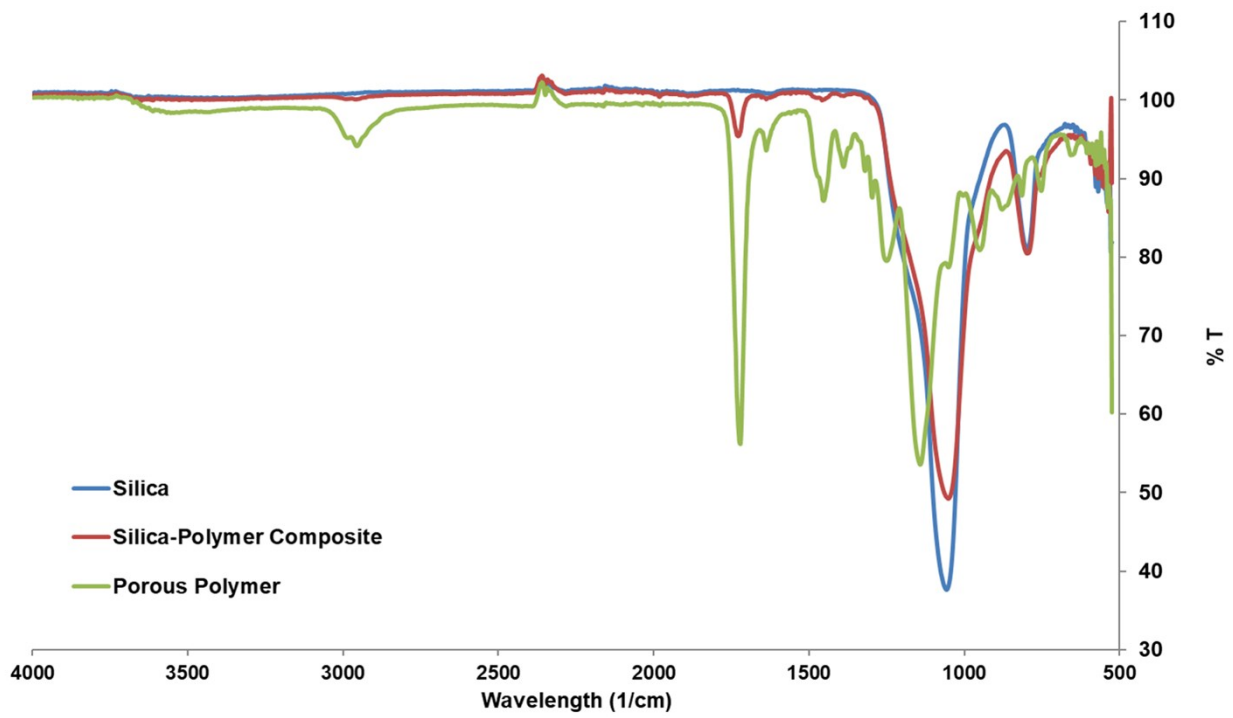


Figure S3. ATR-FTIR spectra of porous silica, silica-polymer composite and porous polymer respectively.

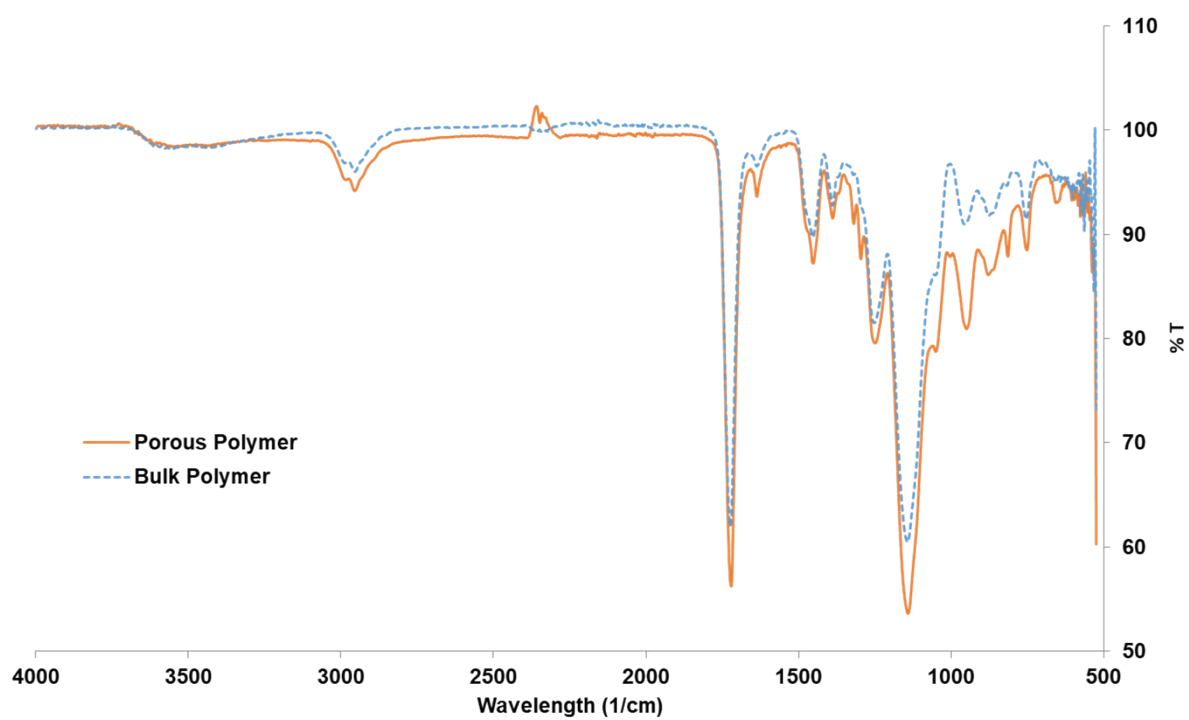


Figure S4. ATR-FTIR overlay spectra of porous microscopic polymer and porous monolith (dotted line).

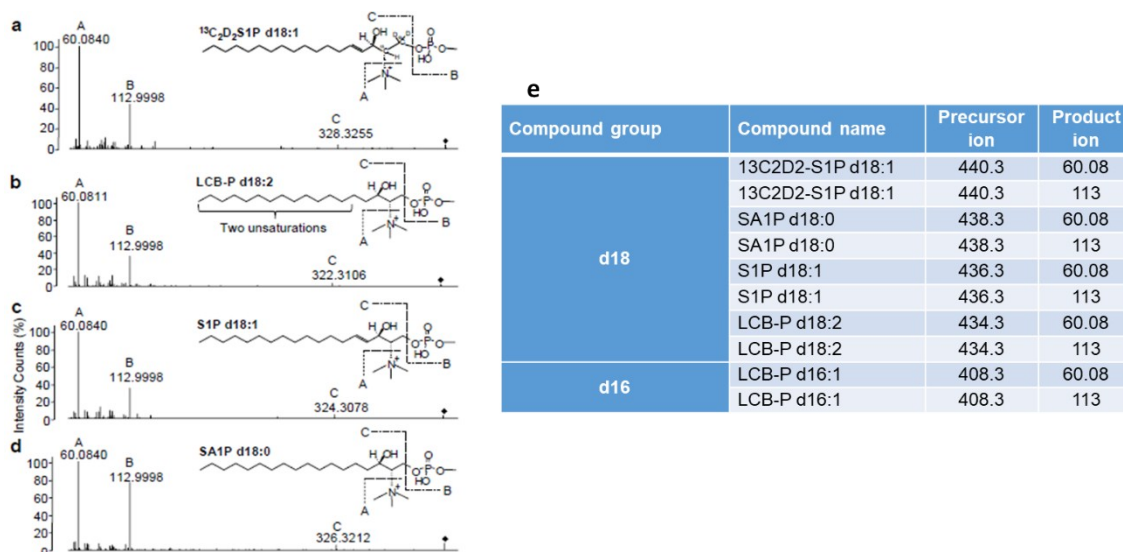


Figure S5. Representative collision-induced dissociation product ion mass spectra (in positive ionization mode) of TMS-derivatized synthetic stable isotope standard (d18:1 $^{13}\text{C}_2\text{D}_2\text{-S1P}$, m/z 440, diamond symbol) yielded expected ions at m/z 60 (fragment A), m/z 113 (fragment B), and m/z 328 (fragment C). The former two fragments are expected to be invariant for LCB-P with different aliphatic compositions which is indeed the case as shown for corresponding product ion spectra of LCB-P d18:2 (b), S1P d18:1 (c), and S1P d18:0 (d), all derived from extracts of human blood plasma and results summarized in table (e).

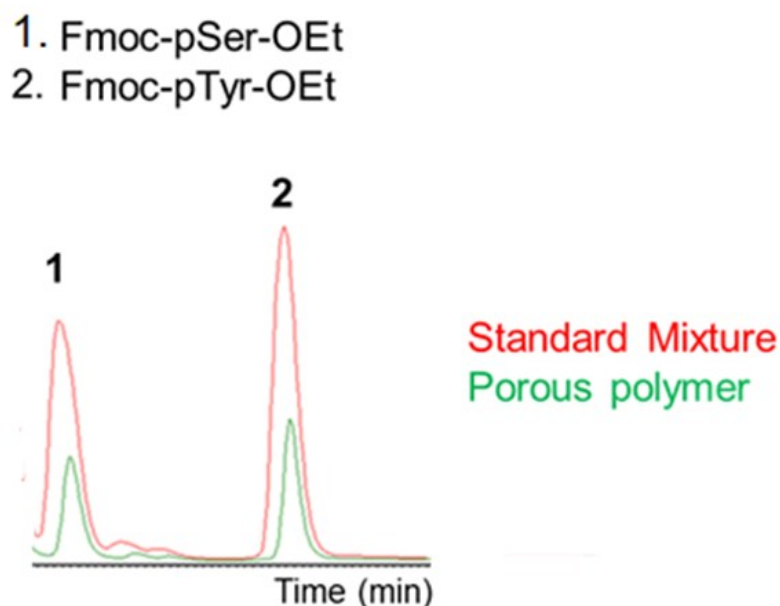


Figure S6. HPLC traces of chromatogram before and after rebinding of an equimolar mixture of Fmoc-pSer-OH, Fmoc-pTyr-OH in 95% MeCN + 0.1% TEA for porous polymer at 254 nm.

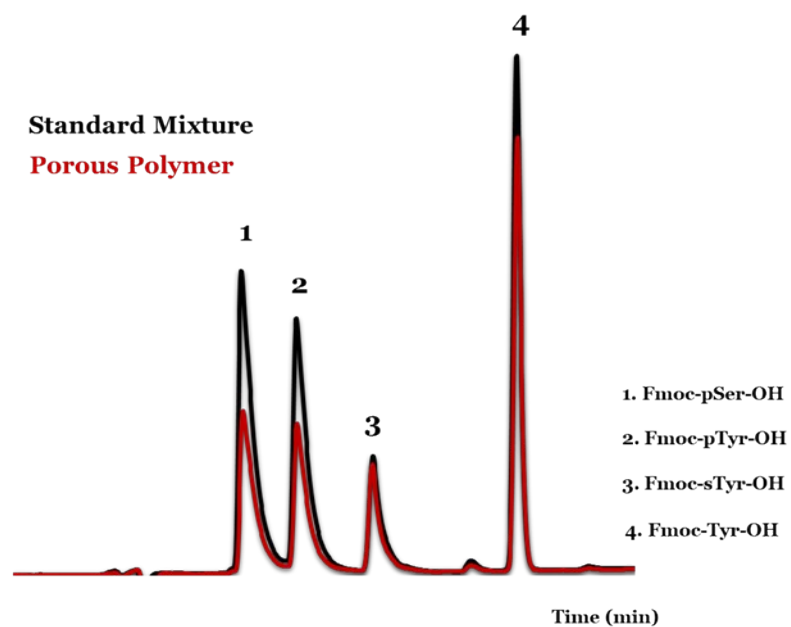


Figure S7. HPLC traces of chromatogram before and after rebinding of Fmoc-pSer-OH, Fmoc-pTyr-OH, Fmoc-sTyr-OH and Fmoc-Tyr-OH in 95% MeCN + 0.1% TEA for porous polymer at 254 nm.

Table S1 Recovery studies of sphingosine-1-phosphate lipids

Relative amounts ¹ of S1P found in flow-through and wash fractions						
	13C ₂ D ₂ -S1P	LCB-P (d16:1)	SA1P (d18:0)	S1P (d18:1)	LCB-P (d18:2)	LPC
Wells	Area	Area	Area	Area	Area	Area
Well 1	438	0	0	209	0	869411
Well 2	2513	0	0	1333	573	891164
Well 3	0	0	0	0	0	896173
Average	984	0	0	514	191	885583
StdDev	1342	0	0	717	331	14227
%RSD	136	0	0	139	173	2
Relative amounts of S1P in 3 elutions						
	13C ₂ D ₂ -S1P	LCB-P (d16:1)	SA1P (d18:0)	S1P (d18:1)	LCB-P (d18:2)	LPC
Wells	Area	Area	Area	Area	Area	Area
Well 1	40796	3240	1487	25448	8117	137437
Well 2	55334	4718	1886	35704	11224	11875
Well 3	50252	4111	1795	29853	10143	17798
Average	48794	4023	1723	30335	9828	55703
StdDev	7378	743	209	5145	1577	70845
%RSD	15	18	12	17	16	127
Relative amounts of S1P in all fractions- Flow through + Wash + elutions						
Wells	13C ₂ D ₂ _S1P	LCB-P (d16:1)	SA1P (d18:0)	S1P (d18:1)	LCB-P (d18:2)	LPC
Well 1	41234	3240	1487	25657	8117	1006848
Well 2	57847	4718	1886	37037	11797	903039
Well 3	50252	4111	1795	29853	10143	913971
Average	49778	4023	1723	30849	10019	941286
StdDev	8317	743	209	5755	1843	57041
%RSD	17	18	12	19	18	6

Note: Well 1, Well 2 and Well 3 are three replicates. SPE experiment was carried out in three different wells of 96 well plate using same amount of the polymer.

Table S2 Enrichment studies of LCB-PS in plasma samples.

Lipid extract of plasma sample (derivatised with TMS), but NOT polymer Enriched						
	13C ₂ D ₂ -S1P	S1P (d16:1)	S1P (d18:0)	S1P (d18:1)	S1P (d18:2)	LPC
Name	Area	Area	Area	Area	Area	Area
Plasma 1	20109	1503	695	11391	4414	787420
Plasma 2	20910	1703	751	12463	4788	761805
Plasma 3	20128	1554	666	11620	4341	729614
Average	20382	1587	704	11825	4514	759613
Std Dev	457	104	43	565	240	28965
%RSD	2	7	6	5	5	4
	13C ₂ D ₂ _S1P	S1P (d16:1)	S1P (d18:0)	S1P (d18:1)	S1P (d18:2)	LPC
Average of plasma (triplicate)	20382	1587	704	11825	4514	759613
Average: Total of 3 elutions (3 wells)	48794	4023	1723	30335	9828	55703
Enrichment Factor	2,39	2,54	2,45	2,57	2,18	0,07

Note: Plasma 1, Plasma 2 and Plasma 3 are three replicates.

¹ Relative amounts of S1P refers to the area under a chromatographic peak