Electronic Supplementary Information for

A Supramolecular cavitand for selective chromatographic separation of peptides using LC-MS/MS: A Combined in silico and Experimental Approach

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S1. Materials and Methods

All chemicals and solvents purchased as a reagent grade, LC-MS grade and used without further purification. Biotage® Intiator sixty microwave used for synthesis of co-pillar[4+1]arene. Perkin Elmer thermogravimetric analyser TGA4000 used for thermogravimetric analysis and Jeol JSM-7100F Field Emission Scanning Electron Microscope (SEM) for structural integrity of new supramolecular stationary phase. YMC Triart HPLC-RPC18 and bare silica columns were purchased from YMC Europe. MS synthetic peptide calibration mix purchased from Sciex. HPLC grade silica was purchased from YMC Europe. LC-MS/MS evaluation of new stationary phase along with RP-C18 and bare silica stationary phase carried out using Eksigent ekspert™ NanoLC 425 coupled with Sciex Triple-TOF™ 5600 mass spectrometer. LC-MS/MS data processed by PeakView™ software.

S2. Computational studies

S2.1 Conformer generation

To generate the different conformers for each of the peptides, we began by drawing a 3D linear structure of the amino acid sequence of the peptide using GaussView 6.0 software. The geometry of this input structure was then optimised and the optimised structure was used to generate the most probable conformers whose energies are within 50 Kcalmol^{-1} of this optimised structure using openbabel. This was done using the following commandline argument.

Obabel <input> -O <output> --confab –nconf 10 --score energy. Details on how to run and use openbabel can be found here. The gas and solvent geometry optimised energies for all conformers can be found in Table 1.

Table 1: Gas and solvent phase geometry optimised energies of all the conformers generated for each peptides.

Conformers /color code		IGNEQGVSR		SAEGLDASASLR		AVGANPEQLTR		VGNEIQYVALR		VFTPLEVDVAK	
		Gas	Solvent	Gas	Solvent	Gas	Solvent	Gas	Solvent	Gas	Solvent
		Energies (Hartree)		Energies (Hartree)		Energies (Hartree)		Energies (Hartree)		Energies (Hartree)	
1	Blue	-172.770	-173.650	-212.428	-213.372	-207.330	-208.275	-224.807	-225.699	-216.483	-217.436
2	Orange	-172.791	-173.682	-212.370	-213.339	-207.342	-208.274	-224.842	-225.739	-216.483	-217.424
3	Green	-172.827	-173.686	-212.415	-213.396	-207.364	-208.287	-224.843	-225.733	-216.604	-217.454
4	Red	-172.855	-173.686	-212.428	-213.374	-207.335	-208.296	-	-	-	-
5	Yellow	-172.827	-173.676	-212.424	-213.36	-	-	-	-	-	-

S2.2 Generation of peptides□pillar[5] arene complexes

All the peptides□pillar[5]arene complexes were generated via a heuristic approach in order to sample all plausible peptides□pillar[5]arene binding sites. This was done by manually changing the position of each peptide conformer inside and around the cavity, while ensuring that all sidechains and terminals of the peptides goes inside the cavity. A minimum of 50 complexes were generated for each conformer depending on the number of plausible interactions that could be sampled. The geometry of these complexes were then optimised in the gas phase using DFTB/mio-1-1 with UFF corrections to dispersion as implemented in ADF version r79006 2019-10-03. Once optimised, 20 lowest energy complexes were then selected and reoptimsed in the solvent using the implicit Generalized Born solvation model with Solvent Accessible Surface Area (GBSA). 2030 surface grid points were used in order to ensure smooth solvent phase geometry optimisation with little

numerical noise as possible. These calculations were done at thesame level of theory as in the gas phase. The gas and solvent phase optmised energies of these complexes, which are presented in Table 3 and 4 respectively, were used to compute the peptides□pillar[5]arene binding energies from equation (1) in the main text. This was done using the optimised energies for each peptide conformer and the energies of the pillar[5]arene (Table 2) .

Table 2: Gas and solvent phase energies pillar[5]arene (Hartree)

Gas (Hartree)	Solvent (Hartree)
-128.91902663	-129.10474038

Table 3a: Gas phase energies (Hartree) of IGNEQGVSR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		orange (Hartree)		Green (Hartree)		Red (Hartree)		Yellow (Hartree)	
Kick35	-301.800146	Kick55	-301.82985	Kick20	-301.788724	Kick30	-301.8374	Kick39	-301.789663
Kick50	-301.796481	Kick48	-301.826716	Kick22	-301.78872	Kick14	-301.834537	Kick71	-301.786777
Kick49	-301.796223	Kick51	-301.81777	Kick4	-301.788709	Kick23	-301.831453	Kick70	-301.786777
Kick48	-301.796194	Kick5	-301.81485	Kick5	-301.788707	Kick24	-301.831451	Kick13	-301.786756
Kick13	-301.791373	Kick4	-301.814607	Kick6	-301.787652	Kick25	-301.831451	Kick25	-301.786685
Kick14	-301.791058	Kick45	-301.814324	Kick3	-301.787035	Kick22	-301.83145	Kick24	-301.786683
Kick36	-301.790877	Kick46	-301.814322	Kick21	-301.786646	Kick16	-301.831336	Kick26	-301.785492
Kick44	-301.787784	Kick49	-301.814298	Kick19	-301.786646	Kick28	-301.828706	Kick67	-301.785445
Kick30	-301.785884	Kick22	-301.8041	Kick23	-301.785702	Kick27	-301.828358	Kick68	-301.785444
Kick40	-301.783016	Kick61	-301.802173	Kick15	-301.784647	Kick29	-301.828245	Kick66	-301.785439
Kick1	-301.78141	Kick28	-301.800776	Kick47	-301.784494	Kick17	-301.827831	Kick77	-301.784981
Kick2	-301.781385	Kick23	-301.79987	Kick27	-301.784069	Kick9	-301.822934	Kick3	-301.784488
Kick43	-301.779419	Kick38	-301.795342	Kick28	-301.784068	Kick20	-301.822584	Kick76	-301.782969
Kick39	-301.779418	Kick24	-301.795174	Kick31	-301.78391	Kick21	-301.822578	Kick51	-301.78279
Kick45	-301.778389	Kick7	-301.794487	Kick25	-301.783905	Kick10	-301.821189	Kick46	-301.782623
Kick37	-301.778336	Kick56	-301.794134	Kick8	-301.783406	Kick2	-301.820733	Kick47	-301.782602
Kick25	-301.777982	Kick6	-301.793286	Kick14	-301.779861	Kick26	-301.819349	Kick79	-301.782537
Kick47	-301.777603	Kick1	-301.793286	Kick7	-301.778276	Kick15	-301.819269	Kick50	-301.782337
Kick27	-301.776595	Kick12	-301.793286	Kick17	-301.778215	Kick18	-301.819268	Kick20	-301.78223
Kick38	-301.776344	Kick11	-301.791527	Kick33	-301.778119	Kick12	-301.818674	Kick53	-301.782105

Table 3b: Gas phase energies (Hartree) of SAEGLDASASLR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)		Red (Hartree)		Yellow (Hartree)	
Kiick26	-341.40727	Kick13	-341.321653	Kick13	-341.371756	Kick29	-341.405503	Kick6	-341.393667
Kiick25	-341.40722	Kick2	-341.320877	Kick12	-341.368592	Kick12	-341.400174	Kick7	-341.391727
Kiick27	-341.405559	Kick19	-341.319705	Kick11	-341.367064	Kick8	-341.399205	Kick14	-341.390021
Kick23	-341.400206	Kick112	-341.318891	Kick10	-341.366046	Kick11	-341.398141	Kick13	-341.387569
Kiick24	-341.398482	Kick3	-341.317235	Kick18	-341.365137	Kick6	-341.396564	Kick5	-341.384562
Kiick38	-341.395745	Kick5	-341.317058	Kick20	-341.364631	Kick10	-341.393457	Kick8	-341.38419
Kiick44	-341.394311	Kick17	-341.316977	Kick31	-341.363246	Kick30	-341.391309	Kick12	-341.38351
Kiick45	-341.392498	Kick21	-341.316209	Kick19	-341.361835	Kick20	-341.38961	Kick11	-341.382216
Kiick40	-341.392484	Kick24	-341.315568	Kick28	-341.361458	Kick7	-341.389393	Kick9	-341.379779
Kiick48	-341.391307	Kick4	-341.315358	Kick29	-341.360072	Kick3	-341.388709	Kick4	-341.37678
Kiick41	-341.390436	Kick22	-341.314714	Kick6	-341.357758	Kick5	-341.386974	Kick24	-341.376239
Kiick50	-341.389976	Kick25	-341.314447	Kick14	-341.35751	Kick4	-341.386462	Kick25	-341.375169
Kiick39	-341.389575	Kick27	-341.314343	Kick3	-341.357167	Kick9	-341.382466	Kick26	-341.375093
Kick12	-341.389097	Kick1	-341.313664	Kick7	-341.357135	Kick14	-341.380068	Kick23	-341.3747
Kiick49	-341.388526	Kick6	-341.312797	Kick5	-341.356093	Kick2	-341.379693	Kick20	-341.372614
Kick11	-341.388314	Kick29	-341.31271	Kick15	-341.356033	Kick16	-341.376402	Kick21	-341.372582
Kick13	-341.38534	Kick7	-341.312383	Kick1	-341.354999	Kick18	-341.375257	Kick22	-341.371039
Kick17	-341.382992	Kick9	-341.311767	Kick4	-341.354826	Kick27	-341.374551	Kick19	-341.365521
Kick10	-341.382516	Kick30	-341.309184	Kick2	-341.354222	Kick23	-341.374082	Kick3	-341.360902
Kiick34	-341.382263	Kick20	-341.308658	Kick30	-341.353393	Kick22	-341.373964	Kick2	-341.356958

Table 3c: Gas phase energies (Hartree) of AVGANPEQLTR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Red (Hartree)	
Kick7	-336.300167	Kick8	-336.305485	Kick25	-336.3041
Kick12	-336.295521	Kick17	-336.300925	Kick30	-336.300155
Kick11	-336.288983	Kick16	-336.29794	Kick29	-336.298132
Kick8	-336.288105	Kick14	-336.29738	Kick31	-336.291554
Kick10	-336.287938	Kick23	-336.292481	Kick28	-336.288801
Kick24	-336.283389	Kick15	-336.292359	Kick27	-336.287685
Kick27	-336.282843	Kick20	-336.285548	Kick10	-336.283116
Kick5	-336.282457	Kick22	-336.284728	Kick37	-336.282191
Kick25	-336.281878	Kick2	-336.279361	Kick24	-336.281796
Kick26	-336.280311	Kick12	-336.2784	Kick9	-336.280305
Kick3	-336.279338	Kick11	-336.277852	Kick23	-336.280244

Kick15	-336.279185	Kick3	-336.277512	Kick22	-336.27729
Kick19	-336.277686	Kick7	-336.276645	Kick8	-336.274623
Kick17	-336.277414	Kick1	-336.276537	Kick26	-336.274133
Kick4	-336.275415	Kick21	-336.275998	Kick14	-336.273187
Kick16	-336.274101	Kick4	-336.275833	Kick20	-336.273138
Kick28	-336.273753	Kick5	-336.275204	Kick13	-336.271607
Kick14	-336.273414	Kick6	-336.271587	Kick6	-336.271469
Kick18	-336.272161	Kick19	-336.270589	Kick3	-336.271353
Kick9	-336.270285	Kick13	-336.270397	Kick18	-336.271274

Table 3d: Gas phase energies (Hartree) of VGNEIQYVALR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)	
Kick33	-353.765955	Kick20	-353.801395	Kick33	-353.806563
Kick28	-353.765831	Kick13	-353.793492	Kick17	-353.804404
Kick38	-353.763295	Kick29	-353.792332	Kick9	-353.803601
Kick39	-353.763036	Kick19	-353.791373	Kick18	-353.801614
Kick40	-353.762496	Kick9	-353.790993	Kick5	-353.794526
Kick37	-353.761256	Kick18	-353.789513	Kick4	-353.792588
Kick22	-353.760859	Kick11	-353.787001	Kick14	-353.792321
Kick27	-353.760472	Kick5	-353.785754	Kick3	-353.792241
Kick43	-353.760304	Kick21	-353.785548	Kick15	-353.792101
Kick11	-353.758634	Kick7	-353.784133	Kick13	-353.791464
Kick24	-353.758514	Kick30	-353.776089	Kick22	-353.790951
Kick23	-353.757552	Kick12	-353.774978	Kick12	-353.790374
Kick21	-353.75674	Kick28	-353.772621	Kick10	-353.788221
Kick42	-353.756679	Kick27	-353.77237	Kick27	-353.787146
Kick26	-353.754149	Kick3	-353.772363	Kick2	-353.785723
Kick10	-353.754111	Kick25	-353.770968	Kick11	-353.784985
Kick20	-353.752803	Kick26	-353.770782	Kick8	-353.784626
Kick4	-353.751572	Kick22	-353.770675	Kick23	-353.782728
Kick5	-353.751217	Kick1	-353.769156	Kick7	-353.778445
Kick29	-353.749735	Kick23	-353.767837	Kick21	-353.77655

Table 3e: Gas phase energies (Hartree) of VFTPLEVDVAK□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)	
Kick6	-345.456348	Kick18	-345.577484	Kick52	-345.565175
Kick24	-345.454154	Kick21	-345.57	Kick8	-345.564356
Kick25	-345.45382	Kick29	-345.565199	Kick10	-345.563801
Kick22	-345.451724	Kick22	-345.564127	Kick9	-345.56348
Kick5	-345.45117	Kick7	-345.563999	Kick7	-345.563477
Kick4	-345.449417	Kick23	-345.562538	Kick6	-345.563195
Kick35	-345.446933	Kick27	-345.562178	Kick51	-345.562963
Kick21	-345.44661	Kick30	-345.562013	Kick5	-345.561439
Kick26	-345.446285	Kick6	-345.558077	Kick40	-345.561384
Kick27	-345.444387	Kick24	-345.556307	Kick39	-345.561248
Kick39	-345.443392	Kick20	-345.555984	Kick4	-345.560175
Kick23	-345.443082	Kick5	-345.555899	Kick49	-345.556346

Kick38	-345.437905	Kick17	-345.552825	Kick47	-345.555996
Kick19	-345.435865	Kick16	-345.549742	Kick34	-345.555598
Kick13	-345.431838	Kick10	-345.548712	Kick33	-345.554621
Kick34	-345.431821	Kick4	-345.547572	Kick46	-345.553887
Kick3	-345.431526	Kick19	-345.547438	Kick32	-345.552999
Kick2	-345.429183	Kick8	-345.546883	Kick30	-345.551862
Kick36	-345.42831	Kick28	-345.545369	Kick20	-345.549685
Kick14	-345.425579	Kick9	-345.544934	Kick25	-345.54739

Table 4a: Solvent phase energies (Hartree) of IGNEQGVSR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)		Red (Hartree)		Yellow (Hartree)	
Kick36	-302.837052	Kick4	-302.841917	Kick20	-302.834498	Kick23	-302.844679	Kick39	-302.838047
Kick37	-302.836664	Kick22	-302.835526	Kick21	-302.834497	Kick25	-302.844556	Kick51	-302.827873
Kick38	-302.835398	Kick11	-302.835135	Kick22	-302.834497	Kick24	-302.844535	Kick53	-302.827869
Kick50	-302.830568	Kick38	-302.83297	Kick19	-302.834496	Kick5	-302.84109	Kick50	-302.827868
Kick49	-302.830151	Kick61	-302.830598	Kick23	-302.834376	Kick3	-302.840369	Kick47	-302.827865
Kick48	-302.826747	Kick23	-302.830065	Kick17	-302.831912	Kick21	-302.83781	Kick46	-302.826648
Kick35	-302.824172	Kick46	-302.828635	Kick14	-302.830718	Kick20	-302.837809	Kick13	-302.820072
Kick47	-302.823253	Kick45	-302.828616	Kick28	-302.828222	Kick15	-302.836159	Kick20	-302.818411
Kick13	-302.819436	Kick51	-302.827942	Kick3	-302.827837	Kick18	-302.836158	Kick67	-302.815973
Kick43	-302.818425	Kick49	-302.827231	Kick7	-302.827246	Kick28	-302.834434	Kick68	-302.81595
Kick39	-302.817816	Kick7	-302.826102	Kick25	-302.815158	Kick16	-302.831263	Kick66	-302.815948
Kick40	-302.817691	Kick28	-302.824929	Kick31	-302.815136	Kick2	-302.830404	Kick71	-302.815253

Table 4b: Solvent phase energies (Hartree) of SAEGLDASASLR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)		Red (Hartree)		Yellow (Hartree)	
Kiick48	-342.531522	Kick112	-342.490259	Kick31	-342.548968	Kick9	-342.530586	Kick8	-342.520956
Kiick45	-342.531186	Kick13	-342.489818	Kick13	-342.54863	Kick29	-342.529751	Kick12	-342.51619
Kiick50	-342.531019	Kick24	-342.487327	Kick12	-342.548017	Kick10	-342.529421	Kick9	-342.515739
Kiick49	-342.529595	Kick25	-342.487118	Kick10	-342.545718	Kick6	-342.52701	Kick14	-342.512612
Kiick44	-342.529518	Kick21	-342.487014	Kick11	-342.545039	Kick16	-342.525597	Kick5	-342.51083
Kiick39	-342.527625	Kick19	-342.486558	Kick29	-342.544102	Kick7	-342.523977	Kick24	-342.509731
Kiick38	-342.527284	Kick30	-342.486315	Kick3	-342.540702	Kick8	-342.520755	Kick21	-342.508878
Kiick40	-342.526742	Kick7	-342.485728	Kick15	-342.538564	Kick3	-342.51996	Kick4	-342.507552
Kick17	-342.525908	Kick29	-342.485575	Kick2	-342.538082	Kick30	-342.519587	Kick6	-342.507473

Kiick27	-342.524381	Kick22	-342.485367	Kick19	-342.537477	Kick11	-342.51883	Kick7	-342.507024
Kiick26	-342.524342	Kick4	-342.484705	Kick30	-342.536272	Kick12	-342.518285	Kick20	-342.506758
Kiick25	-342.524324	Kick2	-342.484537	Kick28	-342.535543	Kick22	-342.516861	Kick13	-342.505782
Kiick24	-342.523713	Kick17	-342.484325	Kick18	-342.535469	Kick23	-342.515287	Kick26	-342.501597
Kiick41	-342.52369	Kick3	-342.48396	Kick20	-342.53353	Kick18	-342.514565	Kick25	-342.501302
Kick23	-342.522897	Kick20	-342.483706	Kick5	-342.533307	Kick27	-342.514546	Kick11	-342.499728
Kiick34	-342.521048	Kick5	-342.483544	Kick14	-342.53312	Kick4	-342.513506	Kick23	-342.499692
Kick13	-342.512573	Kick27	-342.482766	Kick4	-342.532156	Kick5	-342.512014	Kick22	-342.498197
Kick10	-342.5121	Kick6	-342.48109	Kick1	-342.531033	Kick20	-342.510957	Kick3	-342.495583
Kick12	-342.511737	Kick9	-342.479619	Kick6	-342.527596	Kick2	-342.507172	Kick19	-342.485541

Table 4c: Solvent phase energies (Hartree) of AVGANPEQLTR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Red (Hartree)	
Kick12	-337.42054	Kick8	-337.401731	Kick24	-337.432188
Kick11	-337.41838	Kick17	-337.401346	Kick25	-337.430052
Kick7	-337.41777	Kick14	-337.397189	Kick29	-337.427639
Kick8	-337.41755	Kick16	-337.396109	Kick3	-337.425765
Kick10	-337.41583	Kick23	-337.395476	Kick31	-337.424206
Kick27	-337.41466	Kick15	-337.394267	Kick23	-337.424118
Kick9	-337.41407	Kick12	-337.392064	Kick10	-337.423654
Kick26	-337.41399	Kick11	-337.390578	Kick30	-337.422885
Kick28	-337.4131	Kick5	-337.390316	Kick27	-337.422462
Kick5	-337.4103	Kick7	-337.38968	Kick22	-337.421447
Kick15	-337.40977	Kick4	-337.389623	Kick28	-337.420724
Kick17	-337.40893	Kick20	-337.389232	Kick26	-337.419353
Kick16	-337.40847	Kick22	-337.388805	Kick13	-337.41656
Kick19	-337.4083	Kick3	-337.388496	Kick37	-337.415334
Kick25	-337.4079	Kick6	-337.386769	Kick9	-337.413965
Kick18	-337.40674	Kick19	-337.384823	Kick8	-337.412378
Kick24	-337.40637	Kick21	-337.382387	Kick20	-337.411848
Kick14	-337.40483	Kick2	-337.382327	Kick18	-337.411394
Kick3	-337.40441	Kick13	-337.380877	Kick14	-337.404471
Kick4	-337.40429	Kick1	-337.377402	Kick6	-337.403353

Table 4d: Solvent phase energies (Hartree) of VGNEIQYVALR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)	
Kick24	-354.83501	Kick27	-354.87688	Kick9	-354.881279
Kick39	-354.83378	Kick13	-354.87389	Kick11	-354.874717
Kick38	-354.83303	Kick20	-354.87241	Kick18	-354.874144
Kick40	-354.83182	Kick11	-354.87105	Kick17	-354.873733
Kick28	-354.83039	Kick12	-354.86906	Kick8	-354.872439
Kick33	-354.82956	Kick29	-354.86338	Kick5	-354.871574
Kick37	-354.82781	Kick18	-354.86282	Kick33	-354.871426
Kick29	-354.82662	Kick19	-354.86059	Kick2	-354.871394

Kick11	-354.82257	Kick9	-354.8602	Kick4	-354.869499
Kick27	-354.82232	Kick30	-354.85845	Kick10	-354.868848
Kick10	-354.82086	Kick21	-354.8572	Kick15	-354.868563
Kick23	-354.82066	Kick28	-354.85563	Kick3	-354.867259
Kick43	-354.81925	Kick22	-354.85279	Kick22	-354.86528
Kick42	-354.81872	Kick26	-354.85275	Kick7	-354.864864
Kick26	-354.81501	Kick5	-354.85165	Kick23	-354.863103
Kick4	-354.81417	Kick25	-354.85041	Kick12	-354.862209
Kick5	-354.81298	Kick7	-354.85018	Kick13	-354.861513
Kick20	-354.81214	Kick23	-354.84902	Kick21	-354.861234
Kick21	-354.81205	Kick3	-354.84753	Kick14	-354.860991
Kick22	-354.81088	Kick1	-354.84176	Kick27	-354.860649

Table 4e: Solvent phase energies (Hartree) of VFTPLEVDVAK□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

Blue (Hartree)		Orange (Hartree)		Green (Hartree)	
Kick35	-346.6199	Kick18	-346.60532	Kick40	-346.610601
Kick34	-346.6185	Kick20	-346.60421	Kick51	-346.609446
Kick36	-346.6179	Kick21	-346.60171	Kick52	-346.607973
Kick39	-346.6094	Kick22	-346.6014	Kick49	-346.605214
Kick24	-346.6072	Kick23	-346.59551	Kick47	-346.605042
Kick38	-346.6064	Kick24	-346.5876	Kick46	-346.604783
Kick25	-346.6053	Kick29	-346.58103	Kick39	-346.604547
Kick6	-346.6051	Kick19	-346.58025	Kick9	-346.60413
Kick22	-346.6041	Kick27	-346.57979	Kick34	-346.603811
Kick26	-346.6036	Kick28	-346.57905	Kick30	-346.603737
Kick27	-346.6023	Kick30	-346.57872	Kick7	-346.603624
Kick21	-346.6017	Kick7	-346.57635	Kick10	-346.602931
Kick5	-346.6014	Kick17	-346.57473	Kick6	-346.602881
Kick19	-346.6011	Kick16	-346.57459	Kick33	-346.601627
Kick23	-346.6008	Kick5	-346.57378	Kick4	-346.601445
Kick4	-346.6005	Kick6	-346.57364	Kick8	-346.601026
Kick3	-346.5947	Kick4	-346.56978	Kick5	-346.600766
Kick13	-346.5924	Kick10	-346.5664	Kick32	-346.600217
Kick2	-346.5911	Kick8	-346.56435	Kick20	-346.598358
Kick14	-346.5868	Kick9	-346.56354	Kick25	-346.597026

S2.3 Distances of the most important interatomic interaction

Computed distances for all the important interatomic interactions between the peptides and the cavity are presented Table 5. These interactions correspond to interatomic bonds that are less than 3.0 Å. The numbering of each of the atoms can be visualized from any 3D molecular view from their 'xyz' structures provided. The interatomic distances for all the 20 complexes from each peptide conformer can be downloaded from http://doi.org/10.5281/zenodo.3995081

Table 5a: Gas phase interatomic bond distances between peptide and cavity for lowesr energy conformers of IGNEQGVSR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

IGNEQGVSR_Blue			IGNEQGVSR_Green			IGNEQGVSR_Orange			IGNEQGVSR_Red			IGNEQGVSR_Yellow		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_38-H_53	C_168	2.905	C_65-O_1	N_233	2.843	C_65-H_66	O_176	2.822	C_75-O_3	N_134	2.972	C_79-H_82	O_162	2.673
C_38-H_53	O_172	2.25	C_36-C_35	O_223	2.953	C_68-H_70	C_195	2.961	C_65-H_66	O_143	2.473	C_83-H_86	O_161	2.279
C_38-H_54	O_196	2.873	C_37-C_36	O_223	2.782	C_71-H_72	C_168	2.687	C_65-H_66	N_233	2.863	C_102-H_104	O_186	2.981
C_45-H_55	O_212	2.559	C_15-H_48	O_224	2.937	C_71-H_72	O_172	2.854	C_65-H_67	O_223	2.638	C_102-H_105	O_186	2.877
C_61-H_62	C_160	2.98	C_57-H_59	O_224	2.171	C_71-H_72	N_180	2.73	C_75-H_78	N_145	2.749	C_110-N_106	O_162	2.993
C_61-H_62	O_161	2.249	O_2-C_68	O_224	2.953	C_71-H_73	O_186	2.776	C_83-H_84	N_203	2.642	O_162-H_107	C_160	1.947
C_61-H_64	C_219	3	C_68-H_70	C_219	2.518	C_79-H_82	C_192	2.945	C_83-H_86	O_144	2.61	O_162-H_107	O_161	2.336
C_61-H_64	O_223	2.878	C_68-H_70	O_223	2.832	C_79-H_82	O_196	2.172	C_102-H_104	O_224	2.339	O_162-H_107	O_162	1.003
C_65-H_66	N_134	2.958	C_68-H_70	O_224	1.838	C_83-H_86	C_194	2.909	C_110-N_106	O_162	2.904	C_110-H_111	O_161	2.931

C_65-H_67	N_148	2.836	C_79-H_82	O_211	2.938	C_102-H_105	O_144	2.475	O_162-H_107	C_160	1.943	C_113-O_117	N_134	2.734
C_65-H_67	C_152	2.956	C_79-H_82	O_212	2.442	O_162-H_107	C_160	1.931	O_162-H_107	O_161	2.333	C_129-N_127	O_161	2.939
C_65-H_67	C_156	2.993	C_83-H_84	O_196	2.904	O_162-H_107	O_161	2.299	O_162-H_107	O_162	1	C_130-C_129	N_134	2.469
C_65-H_67	O_162	2.765	C_87-H_90	C_219	2.792	O_162-H_107	O_162	0.983	C_110-H_111	O_162	2.977	N_134-C_130	N_134	1.372
C_68-H_70	O_223	2.481	C_87-H_90	O_223	2.125	N_106-H_108	O_162	2.991	C_110-H_111	O_176	2.843	N_134-C_130	C_136	2.467
C_75-H_78	O_223	2.234	C_87-H_90	O_224	2.969	C_110-H_111	C_160	2.945	C_116-H_121	C_175	2.991	C_129-H_132	N_134	2.703
C_83-H_84	O_176	2.073	C_36-H_92	O_223	2.927	C_110-H_111	O_161	2.978	C_116-H_121	O_176	2.601	C_129-H_132	C_195	2.958
C_36-H_92	C_207	2.904	C_102-H_105	C_192	2.726	C_113-O_117	N_134	2.786	C_129-N_127	O_161	2.857	C_130-O_133	N_134	2.286
C_40-H_98	O_161	2.723	C_102-H_105	O_196	2.875	C_129-N_127	O_176	2.857	C_129-N_127	O_176	2.96	C_130-O_133	C_136	2.798
C_102-H_103	O_186	2.818	O_162-H_107	C_160	1.93	N_127-H_128	O_176	1.931	N_127-H_128	O_161	2.72	C_130-O_133	N_163	2.86
C_102-H_104	O_157	2.633	O_162-H_107	O_161	2.302	C_130-C_129	N_134	2.478	N_127-H_128	C_175	2.737	C_130-O_133	N_180	2.862
C_102-H_105	N_180	2.91	O_162-H_107	O_162	0.983	N_134-C_130	N_134	1.367	N_127-H_128	O_176	1.927			
C_102-H_105	O_186	2.732	C_110-H_111	C_160	2.942	N_134-C_130	C_136	2.455	N_127-H_128	N_177	2.951			
O_162-H_107	C_160	1.942	C_110-H_111	O_161	2.853	C_129-H_132	N_134	2.759	C_130-C_129	N_134	2.464			
O_162-H_107	O_161	2.323	C_113-O_117	N_134	2.875	C_130-O_133	N_134	2.272	N_134-C_130	N_134	1.364			
O_162-H_107	O_162	0.983	C_129-N_127	O_176	2.936	C_130-O_133	C_136	2.755	N_134-C_130	C_136	2.458			
N_106-H_108	O_162	2.944	N_127-H_128	O_176	2.03	C_130-O_133	C_139	2.92	C_129-H_131	C_195	2.971			
C_113-O_117	N_134	2.968	C_130-C_129	N_134	2.485	C_130-O_133	N_163	2.954	C_129-H_132	N_134	2.559			
C_130-C_129	N_134	2.481	N_134-C_130	N_134	1.376	C_130-O_133	N_180	2.895	C_130-O_133	N_134	2.282			
N_134-C_130	N_134	1.379	N_134-C_130	C_136	2.447				C_130-O_133	C_136	2.776			
N_134-C_130	C_136	2.451	C_129-H_132	N_134	2.724				C_130-O_133	N_180	2.959			
C_129-H_132	N_134	2.77	C_130-O_133	N_134	2.275									
C_130-O_133	N_134	2.28	C_130-O_133	C_136	2.736									
C_130-O_133	C_136	2.762	C_130-O_133	N_180	2.946									

Table 5b: Gas phase interatomic bond distances between peptide and cavity for lowesr energy conformers of SAEGLDASASLR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

SAEGLDASASLR_Blue			SAEGLDASASLR_Green			SAEGLDASASLR_Orange			SAEGLDASASLR_Red			SAEGLDASASLR_Yellow		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_65-H_67	C_229	2.844	C_65-H_67	O_233	2.207	C_65-O_1	O_233	2.912	C_71-O_4	N_151	2.967	C_65-H_67	N_144	2.483
C_65-H_67	O_233	2.189	C_71-H_73	O_222	2.169	C_65-H_66	O_221	2.565	C_65-H_67	C_156	2.715	C_65-H_67	C_146	2.97
C_65-H_67	C_248	2.767	C_79-H_80	O_212	2.208	C_65-H_66	O_233	2.982	C_65-H_67	O_160	2.415	C_79-H_80	O_180	2.687
C_65-H_67	O_252	2.921	C_79-H_82	N_243	2.889	C_71-H_72	O_221	2.789	C_71-H_72	O_138	2.904	C_83-H_86	C_178	2.94

C_71-H_73	O_221	2.444	C_79-H_82	O_252	2.941	C_83-H_86	C_235	2.968	C_79-H_82	C_147	2.693	C_83-H_86	O_180	2.552
C_79-H_82	O_212	2.981	C_102-H_104	C_251	2.994	C_102-H_104	O_252	2.213	C_79-H_82	O_150	2.06	C_102-H_103	O_150	2.982
C_83-H_86	O_222	2.2	C_102-H_105	N_259	2.978	O_143-H_107	C_137	2.483	C_83-H_84	O_233	2.956	N_106-H_108	C_178	2.797
C_12-H_93	O_252	2.201	C_110-N_106	O_142	2.96	O_143-H_107	C_141	1.992	C_83-H_84	C_248	2.955	N_106-H_108	O_180	2.88
C_33-H_94	O_222	2.967	N_106-H_108	O_142	1.989	O_143-H_107	O_143	0.997	C_83-H_86	O_233	2.633	N_106-H_108	O_181	2.374
C_43-H_96	O_252	2.1	C_113-C_110	O_181	2.921	C_113-O_117	O_143	2.819	C_22-H_100	C_146	2.732	C_121-N_119	O_180	2.948
C_102-H_104	C_248	2.949	C_110-H_111	C_178	2.591	O_116-H_118	O_143	2.74	C_102-H_104	O_160	2.229	O_180-H_120	C_178	1.939
C_102-H_104	O_252	2.756	C_110-H_111	O_180	2.855	C_131-N_129	C_134	2.438	C_102-H_105	O_253	2.802	O_180-H_120	O_180	1.006
O_181-H_107	C_174	2.464	C_110-H_111	O_181	1.789	C_131-N_129	O_138	2.716	C_102-H_105	N_259	2.65	O_180-H_120	O_181	2.345
O_181-H_107	C_178	1.968	C_112-O_116	O_180	2.654	N_129-H_130	C_134	2.719	O_181-H_107	C_174	2.483	C_123-H_125	O_143	2.58
O_181-H_107	O_181	0.998	O_116-H_118	C_178	2.542	N_129-H_130	O_138	2.58	O_181-H_107	C_178	1.976	C_123-H_125	O_180	2.827
C_112-O_116	O_143	2.762	O_116-H_118	O_180	1.634	C_134-C_131	C_134	1.544	O_181-H_107	O_181	0.998	C_131-N_129	C_134	2.487
C_113-O_117	O_181	2.747	O_116-H_118	O_181	2.922	C_134-C_131	C_137	2.573	C_112-O_116	O_143	2.758	C_131-N_129	C_137	2.919
O_116-H_118	C_141	2.76	C_121-N_119	O_142	2.724	C_134-C_131	O_138	2.43	C_113-O_117	O_181	2.749	C_131-N_129	N_144	2.755
O_116-H_118	O_143	1.781	N_119-H_120	C_141	2.387	C_134-C_131	N_144	2.483	O_116-H_118	C_141	2.737	N_129-H_130	C_134	2.898
C_121-H_122	O_191	2.535	N_119-H_120	O_142	1.753	C_131-H_132	C_134	2.193	O_116-H_118	O_143	1.783	N_129-H_130	C_141	2.955
C_123-H_126	O_191	2.668	N_119-H_120	O_143	2.784	C_131-H_132	C_137	2.74	C_121-H_122	O_191	2.49	N_129-H_130	N_144	2.794
C_124-O_128	O_200	2.778	C_123-H_125	O_143	2.769	C_131-H_132	N_144	2.673	C_123-H_126	O_191	2.677	N_129-H_130	C_178	2.824
C_131-N_129	C_134	2.414	C_131-N_129	C_134	2.479	C_137-C_133	C_134	2.549	C_124-O_128	O_200	2.78	N_129-H_130	O_181	2.126
C_131-N_129	O_138	2.649	C_131-N_129	C_137	2.991	C_137-C_133	C_137	1.533	C_131-N_129	C_134	2.433	C_134-C_131	C_134	1.54
N_129-H_130	C_134	2.522	C_131-N_129	O_142	2.715	C_137-C_133	C_141	2.528	C_131-N_129	O_138	2.718	C_134-C_131	C_137	2.59
N_129-H_130	O_138	2.285	C_131-N_129	N_144	2.675				N_129-H_130	C_134	2.636	C_134-C_131	O_138	2.426
C_134-C_131	C_134	1.534	N_129-H_130	C_137	2.821				N_129-H_130	O_138	2.456	C_134-C_131	N_144	2.507
C_134-C_131	C_137	2.575	N_129-H_130	C_141	2.457				C_134-C_131	C_134	1.532	C_131-H_132	C_134	2.17
C_134-C_131	O_138	2.424	N_129-H_130	O_142	1.771				C_134-C_131	C_137	2.577	C_131-H_132	C_137	2.977
C_134-C_131	N_144	2.487	C_134-C_131	C_134	1.539				C_134-C_131	O_138	2.429	C_131-H_132	O_138	2.714
C_131-H_132	C_134	2.175	C_134-C_131	C_137	2.608				C_134-C_131	N_144	2.474	C_137-C_133	C_134	2.505
C_131-H_132	N_144	2.771	C_134-C_131	O_138	2.436				C_131-H_132	C_134	2.181	C_137-C_133	C_137	1.524
C_131-H_132	O_200	2.852	C_134-C_131	N_144	2.481				C_131-H_132	N_144	2.68	C_137-C_133	C_141	2.552
C_137-C_133	C_134	2.568	C_131-H_132	C_134	2.175				C_131-H_132	O_200	2.525	C_137-C_133	O_142	2.817
C_137-C_133	C_137	1.52	C_131-H_132	C_137	2.946				C_137-C_133	C_134	2.541			
C_137-C_133	C_141	2.566	C_131-H_132	O_138	2.797				C_137-C_133	C_137	1.52			
			C_137-C_133	C_134	2.5				C_137-C_133	C_141	2.575			
			C_137-C_133	C_137	1.527									
			C_137-C_133	O_138	2.955									
			C_137-C_133	C_141	2.623									
			C_137-C_133	O_142	2.857									

Table 5c: Gas phase interatomic bond distances between peptide and cavity for lowesr energy conformers of AVGANPEQLTR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

AVGANPEQLTR_Blue			AVGANPEQLTR_Green			AVGANPEQLTR_Orange			AVGANPEQLTR_Red		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_65-O_1	N_194	2.912	C_79-H_82	O_207	2.909	C_102-O_10	O_239	2.885	C_65-H_66	O_178	2.854
C_61-H_62	O_207	2.852	C_83-H_84	O_266	2.253	C_65-H_66	C_265	2.95	C_65-H_66	C_219	2.921
C_71-H_72	C_173	2.914	C_83-H_86	C_265	2.929	C_65-H_66	O_266	2.943	C_65-H_66	C_222	2.976
C_71-H_72	N_179	2.833	C_83-H_86	O_266	2.906	C_65-H_67	C_244	2.965	C_71-H_73	O_178	2.784
C_71-H_73	C_184	2.986	C_83-H_86	O_267	2.867	C_65-H_67	N_263	2.562	C_79-H_80	O_161	2.736
C_71-H_73	O_188	2.827	N_106-H_109	C_206	2.935	C_65-H_67	C_265	2.941	C_33-H_94	O_161	2.36
C_75-H_78	C_206	2.968	N_106-H_109	O_207	2.792	C_71-H_72	O_266	2.717	C_102-H_104	O_140	2.762
C_75-H_78	O_207	2.341	C_112-H_114	C_191	2.81	C_71-H_73	O_238	2.632	C_102-H_105	C_146	2.697
C_79-H_82	C_196	2.894	C_112-H_114	O_193	2.494	C_71-H_73	O_266	2.823	C_102-H_105	O_150	2.848
C_79-H_82	C_199	2.95	C_112-H_115	O_192	2.891	C_83-H_86	O_220	2.062	C_110-N_106	O_220	2.846
O_7-C_83	O_220	2.986	C_112-H_116	O_207	2.58	N_106-H_109	O_193	2.155	C_110-N_106	O_266	2.816
C_83-H_84	O_220	2.206	C_120-N_118	N_134	2.897	C_112-H_114	O_192	2.738	O_117-H_107	C_216	2.461
C_83-H_86	O_203	2.804	C_120-N_118	O_192	2.992	C_112-H_114	O_193	2.927	O_117-H_107	O_220	1.657
C_43-H_96	C_237	2.988	O_192-H_119	C_191	1.933	C_120-N_118	N_134	2.737	N_106-H_109	O_203	2.846
C_19-H_99	O_207	2.965	O_192-H_119	O_192	1.001	C_120-N_118	O_192	2.975	N_106-H_109	N_263	2.879
C_110-N_106	O_192	2.811	O_192-H_119	O_193	2.314	O_192-H_119	C_191	1.933	N_106-H_109	C_265	2.718
O_117-H_107	C_235	2.711	C_123-C_120	N_134	2.5	O_192-H_119	O_192	1.002	N_106-H_109	O_266	1.792
O_117-H_107	O_239	1.735	N_134-C_123	N_134	1.375	O_192-H_119	O_193	2.282	N_118-C_113	O_203	2.536
N_106-H_108	C_265	2.853	N_134-C_123	C_136	2.468	C_123-C_120	N_134	2.491	C_112-H_114	C_206	2.709
N_106-H_108	O_267	2.555	C_122-H_124	N_134	2.974	N_134-C_123	N_134	1.373	C_112-H_114	N_208	2.782
N_106-H_109	C_191	2.57	C_122-H_124	O_192	2.928	N_134-C_123	C_136	2.48	C_112-H_114	O_266	2.589
N_106-H_109	O_192	1.765	C_123-O_127	N_134	2.274	C_122-H_124	C_155	2.964	C_113-O_117	O_203	2.953
N_106-H_109	O_193	2.767	C_123-O_127	C_136	2.773	C_122-H_124	O_192	2.774	C_113-O_117	O_220	2.634
N_106-H_109	O_238	2.949	C_123-O_127	N_141	2.803	C_123-O_127	N_134	2.275	C_120-N_118	O_203	2.703
C_110-H_111	O_266	3	C_125-H_129	C_159	2.973	C_123-O_127	C_136	2.797	N_118-H_119	O_203	2.929
C_110-C_112	O_193	2.994	C_125-H_129	O_161	2.948	C_123-O_127	N_141	2.863	N_118-H_119	O_207	2.565
C_112-H_114	C_191	2.722	C_126-H_131	O_192	2.969	C_126-H_132	N_162	2.962	C_123-C_120	N_134	2.51
C_112-H_114	O_193	1.904	C_126-H_132	N_162	2.931				N_134-C_123	N_134	1.375
C_113-O_117	O_239	2.612							N_134-C_123	C_136	2.447
C_123-C_120	N_134	2.493							C_122-H_124	N_134	2.892
C_120-H_121	N_134	2.657							C_123-O_127	N_134	2.29
N_134-C_123	N_134	1.375							C_123-O_127	C_136	2.781
N_134-C_123	C_136	2.448									
C_123-O_127	N_134	2.288									
C_123-O_127	C_136	2.786									
C_126-H_133	N_134	2.808									

Table 5d: Gas phase interatomic bond distances between peptide and cavity for lowesr energy conformers of VGNEIQYVALR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

VGNEIQYVALR_Blue			VGNEIQYVALR_Green			VGNEIQYVALR_Orange		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_57-H_59	O_141	2.742	C_65-O_1	N_145	2.933	C_65-H_67	C_248	2.88
C_65-H_67	O_140	2.146	C_79-H_82	N_142	2.863	C_65-H_67	O_252	2.283
C_65-H_67	C_147	2.955	C_12-H_93	O_159	2.893	O_4-C_71	O_242	2.984
C_65-H_67	C_149	2.839	C_102-H_105	C_224	2.81	C_71-H_72	O_242	2.625
C_71-H_73	C_136	2.989	N_106-H_107	N_193	2.751	C_71-H_73	O_242	2.791
C_87-H_90	O_141	2.712	O_130-H_108	C_135	2.98	C_79-H_82	O_226	2.152
C_102-H_105	C_150	2.989	O_130-H_108	C_139	2.369	C_83-H_86	N_281	2.897
C_102-H_105	O_154	2.498	O_130-H_108	O_141	2.202	C_87-H_90	O_272	2.857
O_130-H_108	O_158	2.882	N_106-H_109	O_205	2.814	C_26-H_97	O_226	2.452
C_113-O_117	O_158	2.825	C_110-H_111	C_222	2.738	C_102-H_105	N_278	2.817
C_126-H_129	C_157	2.983	C_110-H_111	O_226	2.088	N_106-H_109	C_224	2.901
C_126-H_129	O_159	2.09	C_113-O_117	N_193	2.868	C_112-H_114	N_142	2.842
C_127-O_130	N_145	2.878	C_116-H_121	C_266	2.992	C_113-O_117	N_142	3
C_133-N_131	C_135	2.392	C_116-H_121	O_271	2.934	C_116-H_121	O_192	2.859
C_133-N_131	C_136	2.432	N_124-H_125	C_222	2.976	C_133-N_131	C_135	2.458
C_133-N_131	N_145	2.978	N_124-H_125	O_226	2.042	C_133-N_131	C_136	2.422
O_158-H_132	C_157	1.949	C_127-O_130	C_139	2.86	O_158-H_132	C_157	1.94
O_158-H_132	O_158	0.996	C_127-O_130	O_141	2.944	O_158-H_132	O_158	0.984
O_158-H_132	O_159	2.353	C_133-N_131	C_135	2.462	O_158-H_132	O_159	2.297
C_136-C_133	C_135	1.544	C_133-N_131	C_136	2.406	C_136-C_133	C_135	1.541
C_136-C_133	C_136	1.543	C_133-N_131	C_139	2.964	C_136-C_133	C_136	1.543
C_136-C_133	C_139	2.661	C_133-N_131	O_140	2.692	C_136-C_133	C_139	2.592
C_136-C_133	O_140	2.451	O_158-H_132	C_157	1.935	C_136-C_133	O_140	2.444
C_136-C_133	N_145	2.485	O_158-H_132	O_158	0.983	C_136-C_133	N_145	2.472
			O_158-H_132	O_159	2.306			
			C_136-C_133	C_135	1.55			
			C_136-C_133	C_136	1.536			
			C_136-C_133	C_139	2.528			
			C_136-C_133	O_140	2.437			
			C_136-C_133	N_145	2.485			

Table 5e: Gas phase interatomic bond distances between peptide and cavity for lowesr energy conformers of VFTPLEVDVAK □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

VFTPLEVDVAK_Blue			VFTPLEVDVAK_Green			VFTPLEVDVAK_Orange		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_65-O_1	O_270	2.836	C_65-H_67	O_231	2.128	C_68-O_2	O_205	2.983
C_71-O_4	O_270	2.775	C_71-H_73	O_215	2.245	C_15-C_14	O_205	2.668
C_65-H_67	O_270	2.737	C_79-H_80	O_204	2.378	C_16-C_15	O_205	2.695
C_71-H_73	O_269	2.601	O_232-H_107	C_230	1.93	C_15-H_48	O_205	2.771
C_75-H_78	N_279	2.925	O_232-H_107	O_232	1.001	C_57-H_59	C_203	2.736
C_79-H_82	C_265	2.956	O_232-H_107	O_233	2.322	C_57-H_59	O_204	2.108
C_79-H_82	O_269	2.152	N_106-H_109	O_233	2.487	C_57-H_59	O_205	2.875
C_83-H_84	C_239	2.767	N_106-H_109	O_243	2.692	C_61-H_62	O_204	2.908
C_83-H_84	O_243	2.559	C_113-O_117	O_232	2.764	C_65-H_67	O_200	2.353
C_102-H_104	O_259	2.447	C_116-H_121	O_233	2.989	C_68-H_70	O_205	2.424
C_102-H_105	C_242	2.868	C_116-H_123	O_233	2.454	C_71-H_72	C_214	2.988
C_102-H_105	O_259	2.755	C_129-C_126	N_144	2.476	C_71-H_73	O_200	2.48
C_115-H_118	O_152	2.804	C_126-H_127	N_144	2.534	C_87-H_90	O_204	2.266
C_115-H_118	O_153	2.78	C_132-C_128	C_134	2.539	C_102-H_104	N_206	2.791
C_116-H_123	O_152	2.526	C_132-C_128	C_135	2.538	C_102-H_105	O_181	2.728
C_126-N_124	N_144	2.839	N_144-C_129	N_144	1.372	C_102-H_105	O_215	2.867
C_129-C_126	N_144	2.453	N_144-C_129	C_146	2.461	C_110-H_111	C_230	2.959
C_126-H_127	N_144	2.746	C_128-H_130	C_135	2.759	C_110-H_111	O_233	2.356
C_132-C_128	C_134	2.536	C_128-H_131	C_134	2.654	C_116-H_121	C_230	2.811
C_132-C_128	C_135	2.537	C_135-C_132	C_134	1.408	C_116-H_122	O_153	2.829
N_144-C_129	N_144	1.368	C_135-C_132	C_135	1.407	C_116-H_123	O_153	2.633
N_144-C_129	C_146	2.511	C_135-C_132	C_137	2.437	C_116-H_123	O_232	2.786
C_128-H_130	C_134	2.648	C_135-C_132	C_138	2.437	C_126-N_124	N_144	2.784
C_128-H_131	C_135	2.77	C_135-C_132	C_141	2.819	C_126-N_124	O_232	2.91
C_135-C_132	C_134	1.407	C_129-O_133	N_144	2.287	O_232-H_125	C_230	1.955
C_135-C_132	C_135	1.408	C_129-O_133	C_146	2.825	O_232-H_125	O_232	0.999
C_135-C_132	C_137	2.437				O_232-H_125	O_233	2.34
C_135-C_132	C_138	2.436				C_129-C_126	N_144	2.466
C_135-C_132	C_141	2.818				C_132-C_128	C_134	2.54
C_129-O_133	N_144	2.298				C_132-C_128	C_135	2.533
C_129-O_133	C_146	2.921				N_144-C_129	N_144	1.374
						N_144-C_129	C_146	2.485
						C_128-H_130	C_134	2.667
						C_128-H_130	N_144	2.825
						C_128-H_130	O_243	2.258
						C_128-H_131	C_135	2.683
						C_128-H_131	O_269	2.785
						C_135-C_132	C_134	1.408
						C_135-C_132	C_135	1.408

						C_135-C_132	C_137	2.439
						C_135-C_132	C_138	2.437
						C_135-C_132	C_141	2.821
						C_129-O_133	N_144	2.282
						C_129-O_133	C_146	2.819

Table 5a: Solvent phase interatomic bond distances between peptide and cavity for lowesr energy conformers of IGNEQGVSR□pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

IGNEQGVSR_Blue			IGNEQGVSR_Green			IGNEQGVSR_Orange			IGNEQGVSR_Red			IGNEQGVSR_Yellow		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_79-O_5	O_143	2.971	C_57-H_59	O_224	2.989	C_71-H_73	O_162	2.544	C_71-H_73	O_161	2.825	C_65-H_67	O_211	2.897
C_61-O_9	O_224	2.995	C_68-H_70	O_224	2.467	C_79-H_80	N_177	2.964	C_83-H_84	O_211	2.908	C_79-H_82	O_162	2.842
C_38-H_54	N_233	2.756	C_79-H_82	O_212	2.841	C_79-H_82	O_161	2.994	C_83-H_86	O_211	2.789	C_83-H_86	O_161	2.98
C_79-H_80	O_176	2.67	C_83-H_84	O_196	2.786	C_33-H_94	O_176	2.422	C_26-H_97	N_177	2.815	C_33-H_94	O_161	2.426
C_79-H_82	O_143	2.82	C_102-H_105	O_186	2.843	C_26-H_97	O_161	2.435	O_162-H_107	C_160	1.91	O_162-H_107	C_160	1.905
C_83-H_84	N_180	2.99	C_102-H_105	C_192	2.901	C_22-H_100	O_162	2.883	O_162-H_107	O_161	2.302	O_162-H_107	O_161	2.291
C_87-H_90	O_162	2.947	C_102-H_105	O_196	2.7	C_102-H_103	O_211	2.911	O_162-H_107	O_162	1.003	O_162-H_107	O_162	1.004
C_26-H_97	O_143	2.839	O_162-H_107	C_160	1.894	O_162-H_107	C_160	1.894	C_110-H_111	O_161	2.814	C_110-H_111	O_161	2.614
C_40-H_98	C_232	2.951	O_162-H_107	O_161	2.292	O_162-H_107	O_161	2.291	C_129-N_127	N_134	2.798	C_129-N_127	N_134	2.817
C_40-H_98	N_234	2.791	O_162-H_107	O_162	0.986	O_162-H_107	O_162	0.986	N_127-H_128	N_177	2.971	N_127-H_128	O_161	2.843
C_22-H_100	N_134	2.898	N_106-H_108	C_160	2.964	N_106-H_108	O_161	2.958	C_130-C_129	N_134	2.466	C_130-C_129	N_134	2.468
C_102-H_104	O_157	2.888	N_106-H_108	O_161	2.991	C_110-H_111	O_176	2.601	N_134-C_130	N_134	1.298	N_134-C_130	N_134	1.298
C_102-H_105	O_157	2.898	N_106-H_108	O_162	2.986	C_113-O_117	N_134	2.946	N_134-C_130	C_136	2.439	N_134-C_130	C_136	2.435
C_102-H_105	N_180	2.764	C_110-H_111	O_161	2.843	C_130-C_129	N_134	2.464	C_129-H_132	O_211	2.806	C_129-H_132	O_211	2.774
C_102-H_105	O_186	2.861	C_116-H_121	O_161	2.947	N_134-C_130	N_134	1.298	C_130-O_133	N_134	2.308	C_130-O_133	N_134	2.307
O_162-H_107	C_160	1.894	C_129-N_127	N_134	2.971	N_134-C_130	C_136	2.433	C_130-O_133	C_136	2.795	C_130-O_133	C_136	2.784
O_162-H_107	O_161	2.284	N_127-H_128	O_176	2.245	N_134-C_130	O_212	2.956	C_130-O_133	O_212	2.832			
O_162-H_107	O_162	0.986	C_130-C_129	N_134	2.458	C_129-H_131	O_211	2.974						
C_129-N_127	N_134	2.772	N_134-C_130	N_134	1.298	C_129-H_132	N_134	2.758						
N_127-H_128	N_134	2.829	N_134-C_130	C_136	2.432	C_129-H_132	O_211	2.976						
C_130-C_129	N_134	2.451	C_129-H_132	N_134	2.777	C_129-H_132	O_212	2.921						
N_134-C_130	N_134	1.297	C_130-O_133	N_134	2.31	C_130-O_133	N_134	2.306						
N_134-C_130	C_136	2.45	C_130-O_133	C_136	2.789	C_130-O_133	C_136	2.785						
C_129-H_132	N_134	2.986												
C_130-O_133	N_134	2.313												
C_130-O_133	C_136	2.826												

Table 5b: Solvent phase interatomic bond distances between peptide and cavity for lowesr energy conformers of SAEGLDASASLR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

SAEGLDASASLR_Blue			SAEGLDASASLR_Green			SAEGLDASASLR_Orange			SAEGLDASASLR_Red			SAEGLDASASLR_Yellow		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_65-H_67	O_221	2.564	C_65-H_66	O_150	2.985	C_65-O_1	O_233	2.946	C_65-O_1	O_233	2.961	C_79-H_80	O_180	2.748
C_83-H_86	O_252	2.901	C_65-H_67	O_150	2.567	C_65-H_66	O_221	2.473	C_65-H_67	O_253	2.847	C_102-H_104	O_150	2.532
C_83-H_86	O_253	2.733	C_71-H_72	C_196	2.928	C_102-H_104	O_252	2.745	C_83-H_86	O_222	2.487	N_106-H_108	C_178	2.933
O_181-H_107	C_174	2.52	C_79-H_80	O_233	2.572	C_102-H_105	O_252	2.872	C_12-H_93	C_248	2.87	N_106-H_108	O_180	2.781
O_181-H_107	C_178	1.915	C_83-H_86	O_233	2.902	O_143-H_107	C_137	2.505	C_12-H_93	O_252	2.184	N_106-H_108	O_181	2.854
O_181-H_107	O_181	0.994	C_102-H_103	O_201	2.72	O_143-H_107	C_141	1.912	C_43-H_96	N_243	2.961	O_180-H_120	C_178	1.897
C_112-O_116	O_143	2.867	C_102-H_103	N_259	2.603	O_143-H_107	O_143	0.994	C_43-H_96	O_252	2.261	O_180-H_120	O_180	1.003
C_113-O_117	O_181	2.898	O_117-H_107	C_178	2.922	C_113-O_117	O_143	2.989	O_181-H_107	C_174	2.527	O_180-H_120	O_181	2.278
O_116-H_118	C_141	2.829	O_117-H_107	O_181	1.958	O_116-H_118	O_143	2.772	O_181-H_107	C_178	1.915	C_123-H_125	O_142	2.844
O_116-H_118	O_143	1.865	N_106-H_108	O_142	2.861	C_131-N_129	C_134	2.43	O_181-H_107	O_181	0.995	C_123-H_125	O_181	2.877
C_121-H_122	O_191	2.774	C_112-O_116	O_180	2.864	C_131-N_129	O_138	2.728	C_112-O_116	O_143	2.893	C_123-H_126	O_143	2.886
C_123-H_126	O_191	2.495	C_113-O_117	O_181	2.902	N_129-H_130	C_134	2.703	C_113-O_117	O_181	2.892	C_131-N_129	C_134	2.407
C_124-O_128	O_200	2.853	O_116-H_118	C_178	2.66	N_129-H_130	O_138	2.523	O_116-H_118	C_141	2.836	C_131-N_129	C_137	2.966
C_131-N_129	C_134	2.408	O_116-H_118	O_180	1.861	C_134-C_131	C_134	1.503	O_116-H_118	O_143	1.906	C_131-N_129	N_144	2.723
C_131-N_129	O_138	2.662	O_116-H_118	O_181	2.69	C_134-C_131	C_137	2.564	C_121-H_122	O_191	2.932	N_129-H_130	C_134	2.661
N_129-H_130	C_134	2.483	C_123-H_125	O_143	2.757	C_134-C_131	O_138	2.492	C_123-H_126	O_191	2.418	N_129-H_130	O_142	2.757
N_129-H_130	O_138	2.164	C_131-N_129	C_134	2.397	C_134-C_131	N_144	2.457	C_124-O_128	O_200	2.896	N_129-H_130	N_144	2.63
C_134-C_131	C_134	1.502	C_131-N_129	C_137	2.982	C_131-H_132	C_134	2.138	C_131-N_129	C_134	2.408	N_129-H_130	O_181	2.297
C_134-C_131	C_137	2.574	C_131-N_129	C_141	2.915	C_131-H_132	C_137	2.715	C_131-N_129	O_138	2.659	C_134-C_131	C_134	1.502
C_134-C_131	O_138	2.483	C_131-N_129	N_144	2.739	C_131-H_132	N_144	2.674	N_129-H_130	C_134	2.49	C_134-C_131	C_137	2.589
C_134-C_131	N_144	2.47	N_129-H_130	C_134	2.709	C_137-C_133	C_134	2.502	N_129-H_130	O_138	2.173	C_134-C_131	O_138	2.476
C_131-H_132	C_134	2.141	N_129-H_130	C_141	2.999	C_137-C_133	C_137	1.535	C_134-C_131	C_134	1.501	C_134-C_131	N_144	2.474
C_131-H_132	N_144	2.738	N_129-H_130	O_142	2.853	C_137-C_133	C_141	2.483	C_134-C_131	C_137	2.569	C_131-H_132	C_134	2.144
C_131-H_132	O_200	2.924	N_129-H_130	N_144	2.894				C_134-C_131	O_138	2.483	C_131-H_132	C_137	2.927
C_137-C_133	C_134	2.509	C_134-C_131	C_134	1.504				C_134-C_131	N_144	2.469	C_131-H_132	O_138	2.835
C_137-C_133	C_137	1.534	C_134-C_131	C_137	2.566				C_131-H_132	C_134	2.136	C_137-C_133	C_134	2.48
C_137-C_133	C_141	2.489	C_134-C_131	O_138	2.49				C_131-H_132	N_144	2.736	C_137-C_133	C_137	1.526

			C_134-C_131	N_144	2.464				C_131-H_132	O_200	2.899	C_137-C_133	O_138	2.884
			C_131-H_132	C_134	2.128				C_137-C_133	C_134	2.514	C_137-C_133	C_141	2.537
			C_131-H_132	C_137	2.837				C_137-C_133	C_137	1.531	C_137-C_133	O_142	2.876
			C_131-H_132	O_138	2.979				C_137-C_133	C_141	2.507			
			C_131-H_132	N_144	2.977									
			C_137-C_133	C_134	2.521									
			C_137-C_133	C_137	1.529									
			C_137-C_133	O_138	2.841									
			C_137-C_133	C_141	2.53									
			C_137-C_133	O_142	2.981									

Table 5c: Solvent phase interatomic bond distances between peptide and cavity for lowesr energy conformers of AVGANPEQLTR pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

AVGANPEQLTR_Blue			AVGANPEQLTR_Green			AVGANPEQLTR_Orange			AVGANPEQLTR_Red		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_71-O_4	O_161	2.894	C_83-H_84	N_211	2.85	C_102-O_10	O_239	2.681	C_71-O_4	O_178	2.924
C_44-C_43	O_178	2.896	C_83-H_84	O_220	2.48	C_65-H_66	O_266	2.913	C_65-H_66	O_178	2.971
C_65-H_66	O_161	2.576	C_83-H_86	O_266	2.983	C_65-H_67	N_263	2.931	C_79-H_82	O_193	2.946
C_71-H_72	O_161	2.956	C_33-H_94	N_208	2.944	C_65-H_67	C_265	2.915	C_83-H_86	O_161	2.992
C_71-H_73	O_150	2.636	C_102-H_103	C_136	2.976	C_71-H_72	O_266	2.891	C_33-H_94	O_161	2.416
C_83-H_86	O_188	2.941	C_102-H_104	N_134	2.991	C_71-H_73	O_238	2.874	C_102-H_105	O_150	2.379
C_12-H_93	O_178	2.964	C_112-H_114	O_193	2.876	C_83-H_86	O_220	2.474	O_117-H_107	O_220	2.693
C_22-H_100	O_150	2.823	C_112-H_115	C_191	2.912	N_106-H_109	O_193	2.294	N_106-H_109	O_203	2.517
O_117-H_107	C_235	2.985	C_112-H_115	O_192	2.555	C_112-H_114	O_192	2.78	N_106-H_109	O_220	2.969
O_117-H_107	O_239	2.401	C_112-H_116	C_202	2.993	C_112-H_114	O_193	2.969	N_106-H_109	O_266	2.751
N_106-H_108	O_238	2.953	C_112-H_116	C_206	2.995	C_120-N_118	N_134	2.87	C_112-H_114	C_202	2.95
N_106-H_108	O_267	2.809	C_112-H_116	O_207	2.321	C_120-N_118	O_192	2.999	C_112-H_114	O_203	2.835
N_106-H_109	C_191	2.959	C_120-N_118	N_134	2.968	O_192-H_119	C_191	1.901	C_112-H_114	O_266	2.748
N_106-H_109	O_192	2.813	C_120-N_118	O_192	2.973	O_192-H_119	O_192	1.003	C_112-H_116	O_266	2.857
N_106-H_109	O_193	2.442	O_192-H_119	C_191	1.907	O_192-H_119	O_193	2.286	C_120-N_118	N_134	2.979
C_110-H_111	O_266	2.976	O_192-H_119	O_192	1.001	C_123-C_120	N_134	2.475	N_118-H_119	O_207	2.977
C_112-H_114	N_162	2.96	O_192-H_119	O_193	2.299	N_134-C_123	N_134	1.296	C_123-C_120	N_134	2.495
C_112-H_114	O_193	2.676	C_123-C_120	N_134	2.481	N_134-C_123	C_136	2.441	N_134-C_123	N_134	1.295
C_123-C_120	N_134	2.47	N_134-C_123	N_134	1.296	C_122-H_124	O_192	2.805	N_134-C_123	C_136	2.413

C_120-H_121	N_134	2.602	N_134-C_123	C_136	2.431	C_123-O_127	N_134	2.312	C_123-O_127	N_134	2.308
N_134-C_123	N_134	1.296	C_122-H_124	N_134	2.894	C_123-O_127	C_136	2.809	C_123-O_127	C_136	2.752
N_134-C_123	C_136	2.425	C_122-H_124	O_192	2.861	C_126-H_132	N_162	2.937			
C_123-O_127	N_134	2.31	C_123-O_127	N_134	2.308						
C_123-O_127	C_136	2.777	C_123-O_127	C_136	2.786						
C_126-H_133	N_134	2.978	C_125-H_129	O_161	2.934						
			C_126-H_131	O_192	2.821						

Table 5d: Solvent phase interatomic bond distances between peptide and cavity for lowesr energy conformers of VGNEIQYVALR pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

VGNEIQYVALR_Blue			VGNEIQYVALR_Green			VGNEIQYVALR_Orange		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_71-O_4	O_158	2.722	C_65-H_66	O_154	2.58	C_79-H_80	O_141	2.502
C_65-H_66	O_159	2.885	C_71-H_72	O_154	2.972	C_79-H_80	N_193	2.901
C_79-H_82	N_145	2.862	C_79-H_80	O_141	2.411	N_106-H_107	C_224	2.82
C_79-H_82	O_154	2.707	C_83-H_84	C_224	2.961	C_116-H_121	N_142	2.906
C_83-H_86	O_141	2.89	N_106-H_107	O_192	2.857	C_127-O_130	C_136	2.995
C_33-H_94	O_141	2.973	N_106-H_109	O_205	2.921	C_133-N_131	C_135	2.478
C_26-H_97	O_154	2.597	C_110-H_111	O_205	2.607	C_133-N_131	C_136	2.45
C_133-N_131	C_135	2.478	C_110-H_111	O_226	2.437	C_133-N_131	O_140	2.986
C_133-N_131	C_136	2.431	C_115-H_118	O_226	2.575	O_158-H_132	C_157	1.896
C_133-N_131	N_145	2.86	C_116-H_121	C_266	2.997	O_158-H_132	O_158	0.986
O_158-H_132	C_157	1.887	C_116-H_122	O_271	2.854	O_158-H_132	O_159	2.294
O_158-H_132	O_158	0.986	C_116-H_123	O_226	2.76	C_136-C_133	C_135	1.539
O_158-H_132	O_159	2.288	N_124-H_125	O_226	2.552	C_136-C_133	C_136	1.503
C_136-C_133	C_135	1.536	C_133-N_131	C_135	2.466	C_136-C_133	C_139	2.547
C_136-C_133	C_136	1.503	C_133-N_131	C_136	2.417	C_136-C_133	O_140	2.482
C_136-C_133	C_139	2.516	C_133-N_131	O_140	2.729	C_136-C_133	N_145	2.458
C_136-C_133	O_140	2.486	O_158-H_132	C_157	1.888			
C_136-C_133	O_141	2.919	O_158-H_132	O_158	0.986			
C_136-C_133	N_145	2.467	O_158-H_132	O_159	2.282			
			C_136-C_133	C_135	1.556			
			C_136-C_133	C_136	1.502			
			C_136-C_133	C_139	2.519			
			C_136-C_133	O_140	2.472			
			C_136-C_133	N_145	2.466			

Table 5e: Solvent phase interatomic bond distances between peptide and cavity for lowesr energy conformers of VFTPLEVDVAK □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

VFTPLEVDVAK_Blue			VFTPLEVDVAK_Green			VFTPLEVDVAK_Orange		
Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)	Peptides	Cavity	BL (A)
C_68-H_70	O_205	2.73	C_65-H_67	C_196	2.915	C_83-O_7	O_181	2.827
C_71-H_72	O_215	2.956	C_65-H_67	O_200	2.863	C_57-H_59	O_204	2.855
C_71-H_73	O_215	2.82	C_79-H_82	C_227	2.894	C_57-H_59	O_205	2.889
C_75-H_78	O_205	2.527	C_79-H_82	O_231	2.991	C_65-H_67	O_200	2.65
C_87-H_90	O_204	2.55	C_79-H_82	N_234	2.883	C_68-H_70	O_205	2.65
C_12-H_93	O_181	2.576	C_83-H_86	O_215	2.666	C_87-H_90	O_204	2.871
C_33-H_94	O_200	2.845	C_26-H_97	O_231	2.693	C_43-H_96	O_200	2.981
C_43-H_96	N_172	2.914	C_102-H_105	O_204	2.796	C_102-H_104	C_196	2.991
C_22-H_100	O_215	2.862	O_232-H_107	C_230	1.9	C_102-H_104	O_200	2.688
C_102-H_104	O_171	2.701	O_232-H_107	O_232	0.995	C_102-H_105	O_181	2.84
C_102-H_105	O_171	2.69	O_232-H_107	O_233	2.283	C_110-H_111	O_233	2.794
C_115-H_118	O_152	2.999	N_106-H_109	O_233	2.808	C_115-H_118	O_153	2.855
C_115-H_118	O_153	2.53	N_106-H_109	O_243	2.897	C_116-H_121	C_230	2.809
C_116-H_123	O_152	2.68	C_113-O_117	O_232	2.936	C_116-H_121	O_233	2.885
C_126-N_124	N_144	2.759	C_116-H_123	O_233	2.678	C_116-H_122	O_153	2.894
C_129-C_126	N_144	2.438	C_129-C_126	N_144	2.462	C_116-H_123	O_153	2.573
C_126-H_127	C_135	2.921	C_126-H_127	N_144	2.582	C_116-H_123	O_232	2.7
C_126-H_127	N_144	2.884	C_132-C_128	C_134	2.541	C_126-N_124	N_144	2.874
C_132-C_128	C_134	2.543	C_132-C_128	C_135	2.542	C_126-N_124	O_232	2.885
C_132-C_128	C_135	2.537	N_144-C_129	N_144	1.295	O_232-H_125	C_230	1.92
N_144-C_129	N_144	1.297	N_144-C_129	C_146	2.428	O_232-H_125	O_232	1
N_144-C_129	C_146	2.463	C_128-H_130	C_135	2.769	O_232-H_125	O_233	2.329
C_128-H_130	C_134	2.648	C_128-H_131	C_134	2.65	C_129-C_126	N_144	2.469
C_128-H_131	C_135	2.769	C_135-C_132	C_134	1.41	C_126-H_127	C_135	2.968
C_135-C_132	C_134	1.409	C_135-C_132	C_135	1.41	C_132-C_128	C_134	2.535
C_135-C_132	C_135	1.41	C_135-C_132	C_137	2.442	C_132-C_128	C_135	2.536
C_135-C_132	C_137	2.441	C_135-C_132	C_138	2.441	N_144-C_129	N_144	1.296
C_135-C_132	C_138	2.441	C_135-C_132	C_141	2.825	N_144-C_129	C_146	2.432
C_135-C_132	C_141	2.824	C_129-O_133	N_144	2.312	C_128-H_130	C_134	2.62

C_129-O_133	N_144	2.316	C_129-O_133	C_146	2.794	C_128-H_130	N_144	2.924
C_129-O_133	C_146	2.861				C_128-H_130	O_232	2.998
						C_128-H_130	O_243	2.378
						C_128-H_131	C_135	2.754
						C_128-H_131	O_269	2.783
						C_135-C_132	C_134	1.408
						C_135-C_132	C_135	1.41
						C_135-C_132	C_137	2.44
						C_135-C_132	C_138	2.44
						C_135-C_132	C_141	2.822
						C_129-O_133	N_144	2.312
						C_129-O_133	C_146	2.79

S2.4 Coordinates of all molecules

The coordinates of all the optimized structures presented in the above tables can be downloaded from http://doi.org/10.5281/zenodo.3995081

S2.5 Specific peptides□pillar[5]arene binding sites

To further elucidate the specific interaction site between the peptide and the cavity, Table 6 presents all the amino acid units that are interacting with the cavity for each conformer. The strength of these interactions can be inferred from Fig 2b in the main text.

Table 6 : Specific amino acid interaction units between cavity and peptides for solvated phase.

Peptides	Description of specific interacting units of each conformer with the cavity				
	Blue	Orange	Green	Red	Yellow
IGNEQGVSR	The glutamic acid (E) unit is fully inserted into the cavity.	The Isoleucine unit (I) at the head of the peptide is fully inserted into the cavity.	The carboxylate unit found on the terminal argenine unit (R) is partially inserted into the cavity.	The Isoleucine unit (I) at the head of the peptide is fully inserted into the cavity.	The Isoleucine unit (I) at the head of the peptide is fully inserted into the cavity.
SAEGLDASASLR	The terminal leucine (L) unit closest to the argenine (R) unit is fully inserted into the cavity.	The terminal leucine (L) unit closest to the argenine (R) unit is halfway inserted into the cavity.	None of the amino acid units are inserted into the cavity. All interactions are at the exterior of the cavity.	The terminal leucine (L) unit closest to the argenine (R) unit is fully inserted into the cavity.	The Serine unit (S) at the head of the peptide is halfway inserted into the cavity.
AVGANPEQLTR	Proline (P) unit	The threonine	The Alanine-	Proline (P) unit	-

	halfway inserted in the cavity.	unit (T), closest to the argenine (R) is halfway inserted into the cavity.	valine (A-V) peptide bond is partially inserted into the cavity.	halfway inserted into the cavity.	
VGNEIQYVALR	The valine and the glycine head (V-G) are inserted in the cavity.	Here the Valine (V) at the head is halfway inserted in the cavity.	Glutamic acid (E) fully inserted in the cavity.	-	-
VFTPLEVDVAK	The glutamic acid (E) unit is fully inserted into the cavity.	The glutamic acid (E) unit is fully inserted into the cavity.	The Valine (V) unit, which is closest to the glumatic acid (L-E-V), is fully inserted into the cavity.	-	-

S3. Synthesis of co-pillar[4+1]arene using microwave irradiation.

Microwave synthesis of co-pillar[4+1]arene incorporating two 8-bromo-octyl substituents was followed out recent developed procedure.[1]

S4 Co-pillar[4+1]arene bonded silica gel HPLC stationary phase

S4.1 Synthesis of co-pillar[4+1]arene bonded silica gel HPLC stationary phase

3 g of YMC Triart HPLC silica grade (particle size 5 µm and pore size is 120Å) was stirred overnight at room temperature in a mixture of THF and TEA (1:1, 50 ml). The solvent mixture was evaporated, and the solid residue dried under room temperature in the fume hood. Later 1.0 gm of co-pillar[4+1]arene was dissolved in dichloromethane (50 mL) and added to the dried basified silica for HPLC stationary phase and stirred overnight at room temperature. The dichloromethane was evaporated and the co-pillar[4+1]arene bonded silica gel stationary phase was washed with DCM to remove unreacted materials and dried for overnight in the fume hood. TGA analysis was carried out to find out % of mass loading of co-pillar[4+1]arene on the surface of HPLC grade silica gel. Thermogravimetric analysis studies confirmed the mass loading of the co-pillar[4+1]arene at 19.1037 % w/w.

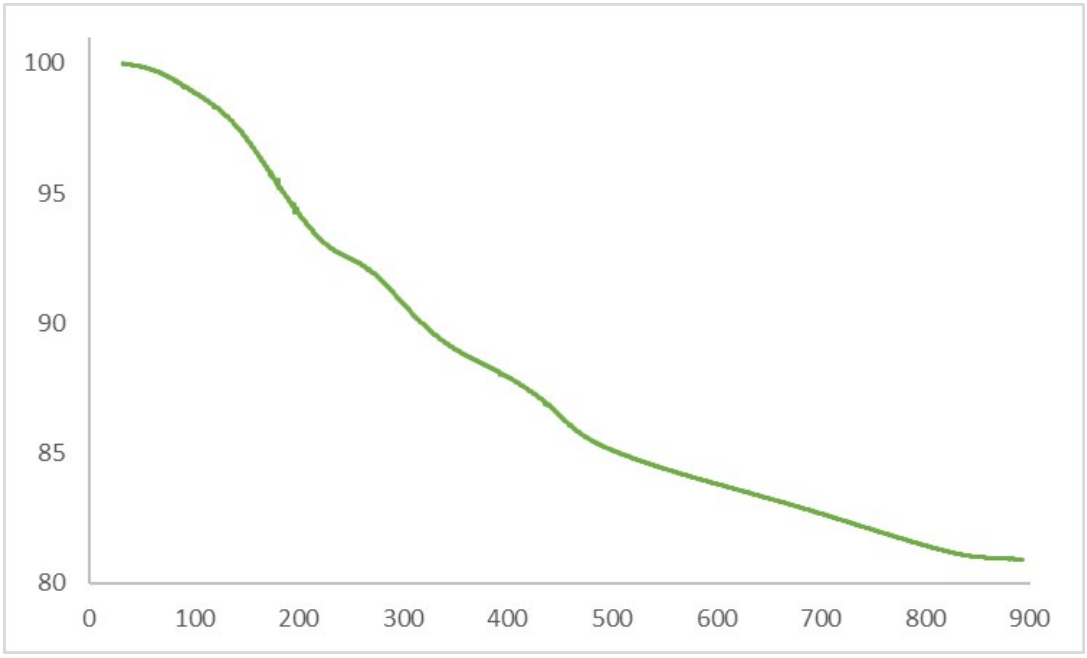

Fig. S1. Thermogravimetric analysis of co-pillar[4+1]arene bound-silica stationary phase.

S4.2 Microscopic imaging of stationary phase silica particles

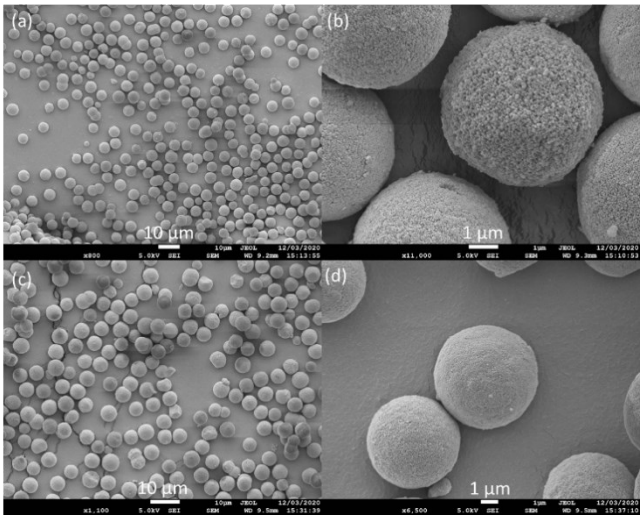

Fig. S2. SEM images showing silica 5 µm particles at (a) 10 and (b) 1 µm magnification and silica functionalized with co-pillar[4+1]arene stationary phase particles at (c) 10 and (d) 1 µm magnification.

S4.3 Column packing of co-pillar[4+1]arene bonded silica gel HPLC stationary phase

Co-pillar[4+1]arene bonded silica gel HPLC stationary phase was packed into a HPLC column using a wet slurry packing method by YMC Europe with column dimensions of 12 nm S-5 µm 150 x 0.3 mm with 1/32" fitting. After packing the column, it was conditioned with water: acetonitrile (1:1) and supplied back for chromatographic studies. Prior to chromatographic experiments, the newly packed HPLC columns were flushed with water: acetonitrile (1:1) to condition the column. The eluents were collected at different columns volumes to identify the elution of co-pillar[5]arene from the silica-bound co-pillar[5]arene HPLC stationary phase. There was no observation of co-pillar[4+1]arene eluting from the column even after 100 column volumes.

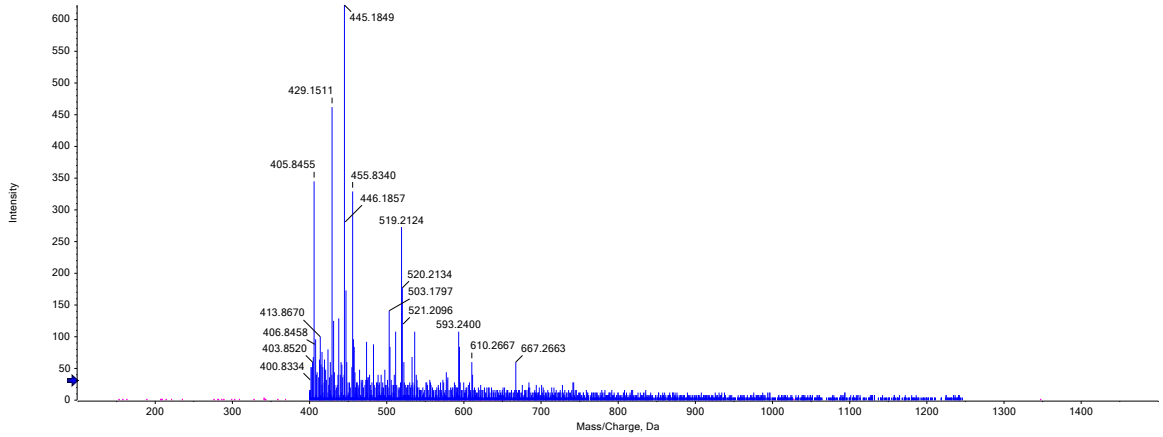

Fig. S3. LC-MS spectrum of eluent from silica-bound co-pillar[4+1]arene stationary phase at 1 column volume.

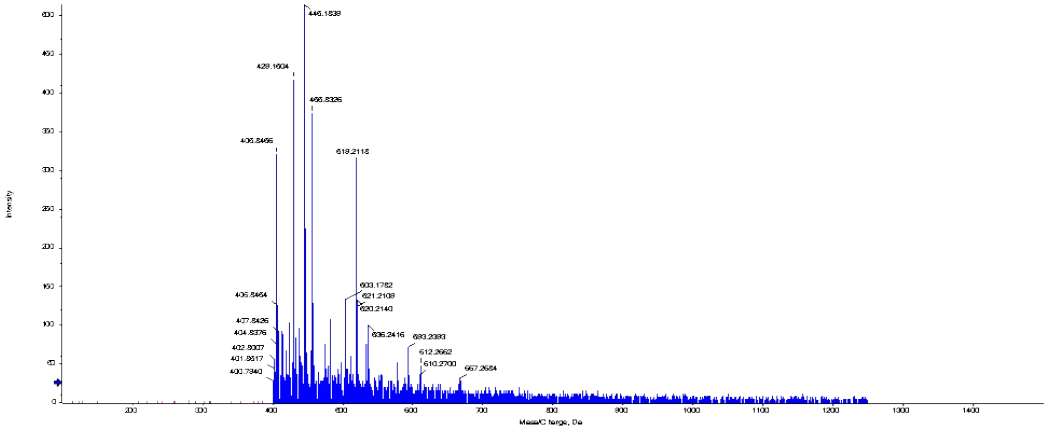

Fig. S4. LC-MS spectrum of eluent from silica-bound co-pillar[4+1]arene stationary phase at 50 column volumes.

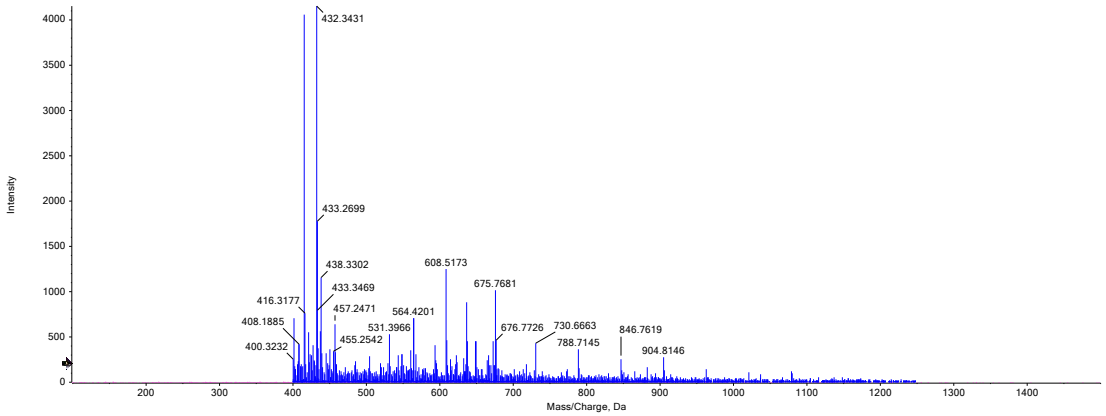

Fig. S5. LC-MS spectrum of eluent from silica-bound co-pillar[4+1]arene stationary phase at 100 column volumes.

S5 LC-MS/MS separation of peptides on RP-C18, co-pillar[4+1]arene bonded-silica gel stationary phase and bare silica.

LC-MS/MS analysis of five selected peptides from a peptide calibration mix was used to evaluate the performance of the newly synthesised co-pillar[4+1]arene silica bound HPLC chromatographic stationary phase in comparison with RP-C18 and a bare silica phase. Gradient conditions on bare silica phase are the same as those of mobile phase gradient conditions for co-pillar[4+1]arene bound silica gel stationary phase column as bare silica phase has been used as negative control.

S5.1. LC-MS/MS analysis of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK on co-pillar[4+1]arene bound-silica HPLC stationary phase

Flow rate: RP-C18-7.5 µL min-1
Column Temperature: 30°C
Column Dimensions: 12 nm S-5 um 150 x 0.3 mm with 1/32" fitting
Mobile Phase: solvent A: water + 0.1% formic acid
solvent B: acetonitrile + 0.1% formic acid
Peptides: IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK
Mobile phase gradient conditions:

Time (min)	%A	%B
0.0	97	03
5.5	92	08
7.0	20	80
10	20	80
11	97	03
13	97	03

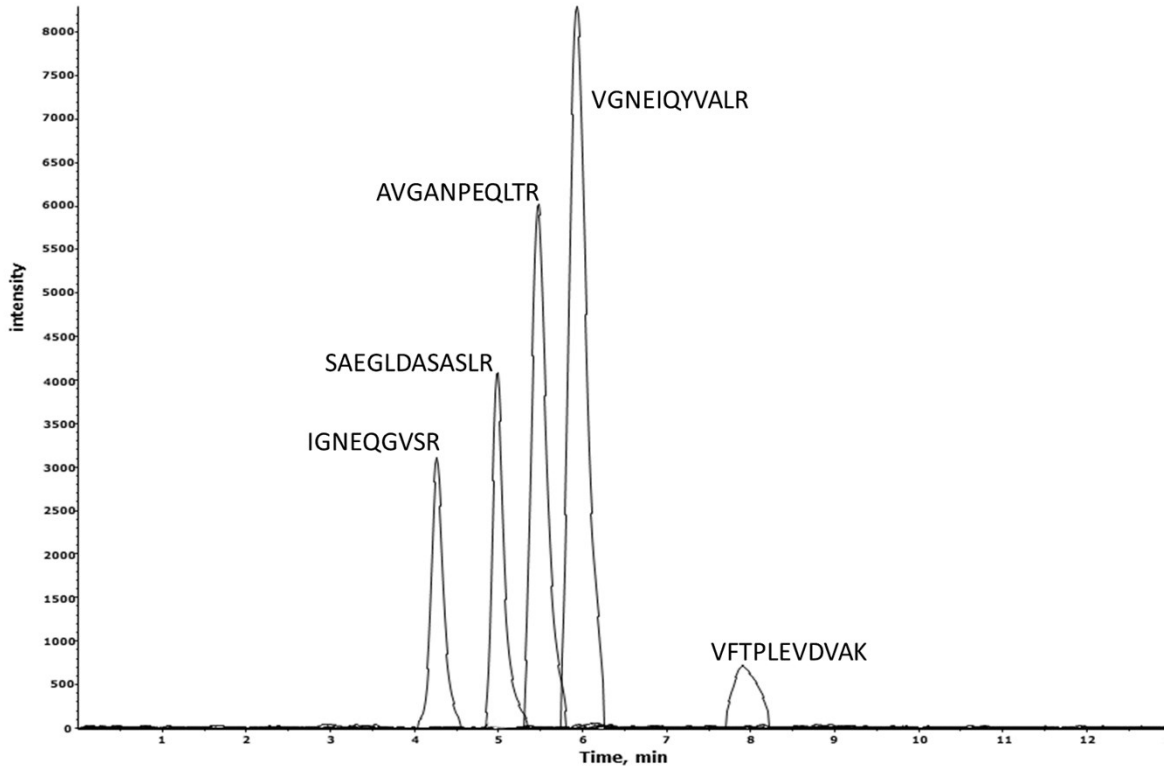

Fig.S6. LC-MS/MS Separation of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK on silica-bound co-pillar[4+1]arene HPLC stationary phase.

S5.2. LC-MS/MS analysis of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK on RP-C18 HPLC column

Flow rate: RP-C18-7.5 µL min-1
Column Temperature: 30°C
Column Dimensions: 12 nm S-5 um 150 x 0.3 mm with 1/32" fitting
Mobile Phase: solvent A: water + 0.1% formic acid
solvent B: acetonitrile + 0.1% formic acid
Peptides: IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK

Time (min)	%A	%B
0.0	97	03
5.5	92	08
7.0	20	80
10	20	80
11	97	03
13	97	03

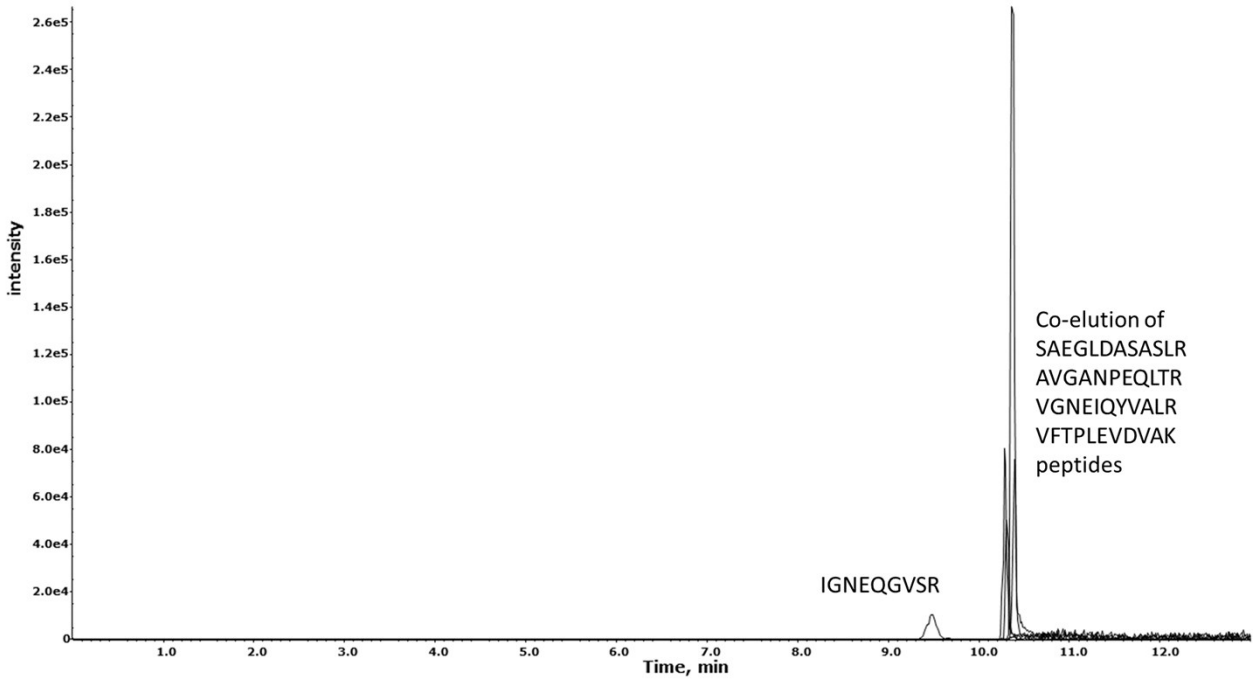

Fig. S7. LC-MS/MS separation of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK peptides on RP-C18 HPLC stationary phase.

S5.3. LC-MS/MS separation of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK peptides on normal phase HPLC column

Flow rate: RP-C18-7.5 µL min-1
Column Temperature: 30°C
Column Dimensions: 12 nm S-5 um 150 x 0.3 mm with 1/32" fitting
Mobile Phase: solvent A: water + 0.1% formic acid
solvent B: acetonitrile + 0.1% formic acid
Peptides: IGNEQGVSR, SAEGLDASASLR,
AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK

Time (min)	%A	%B
0.0	97	03
5.5	92	08
7.0	20	80
10	20	80
11	97	03
13	97	03

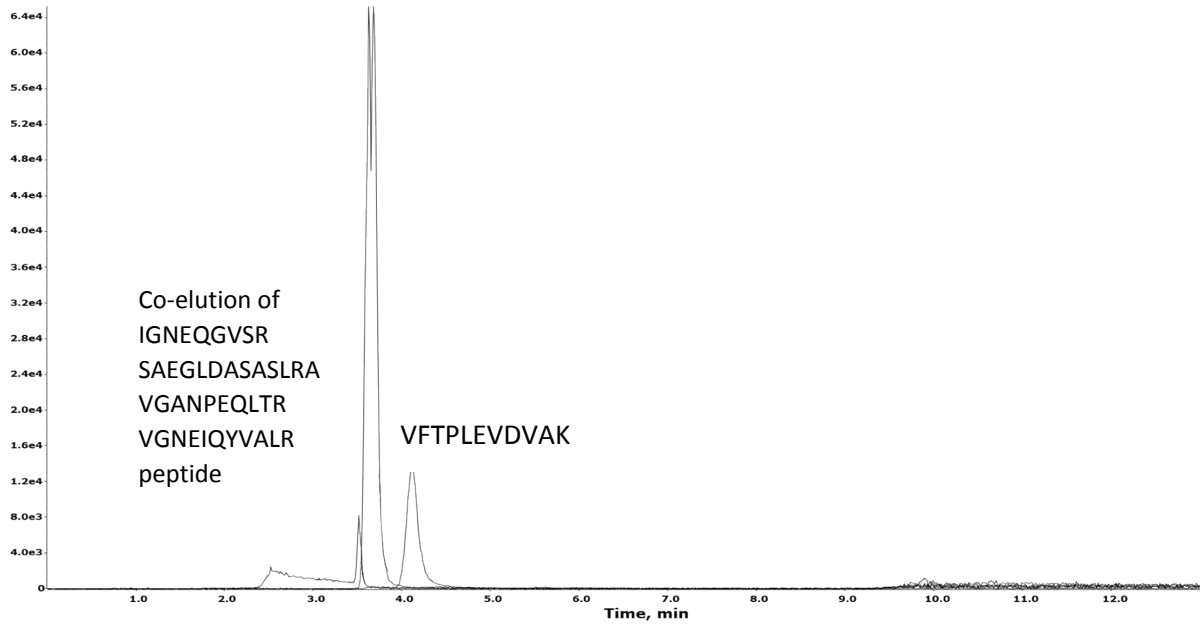

Fig.S8. LC-MS/MS separation of IGNEQGVSR, SAEGLDASASLR, AVGANPEQLTR, VGNEIQYVALR and VFTPLEVDVAK peptides on normal phase silica HPLC stationary phase.

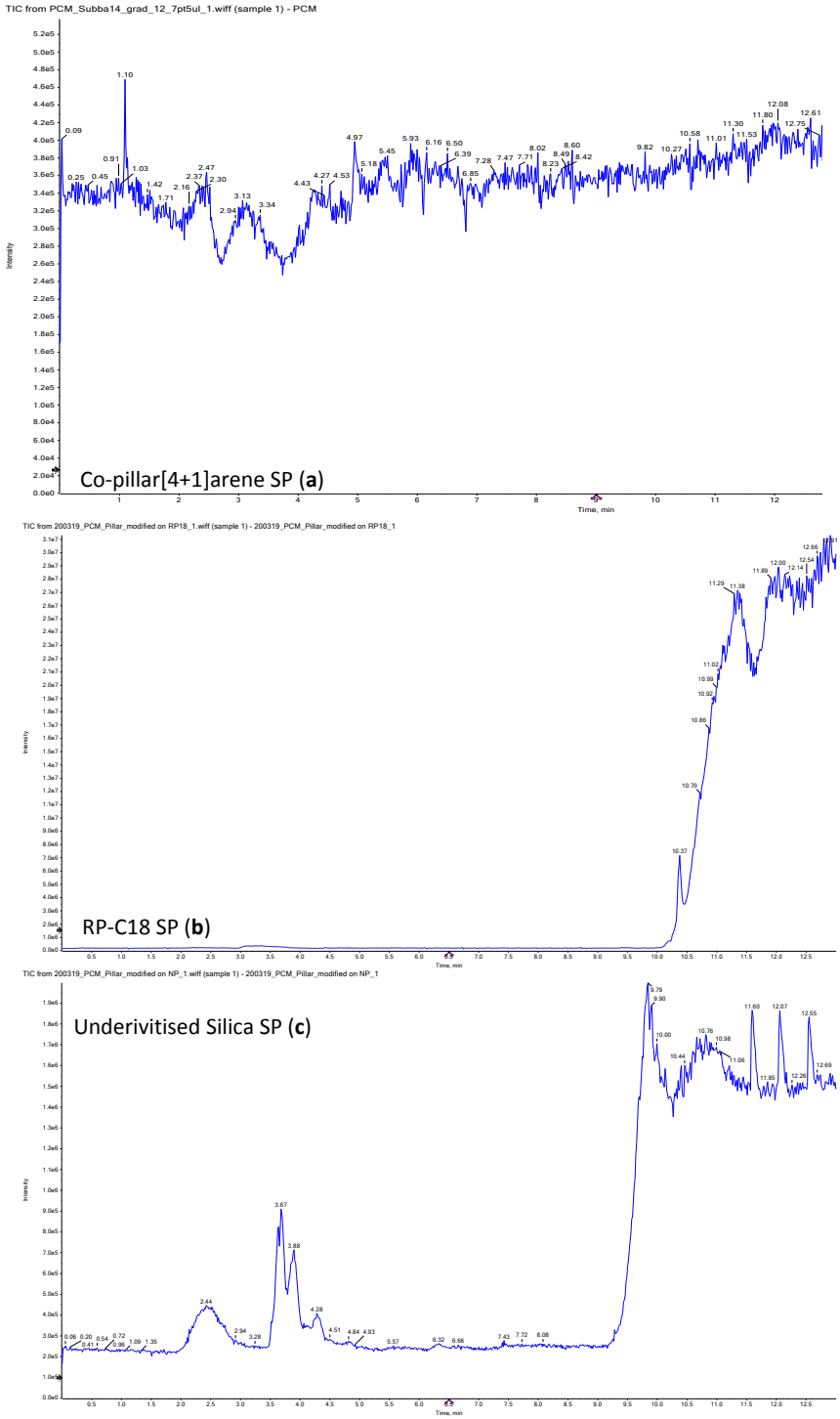

Fig.S9. Total ion chromatogram from full scan data acquisition of Peptide Cal

Mix on (a) co-pillar[4+1]arene SP, (b) RP-C18 column and (c) normal phase column.

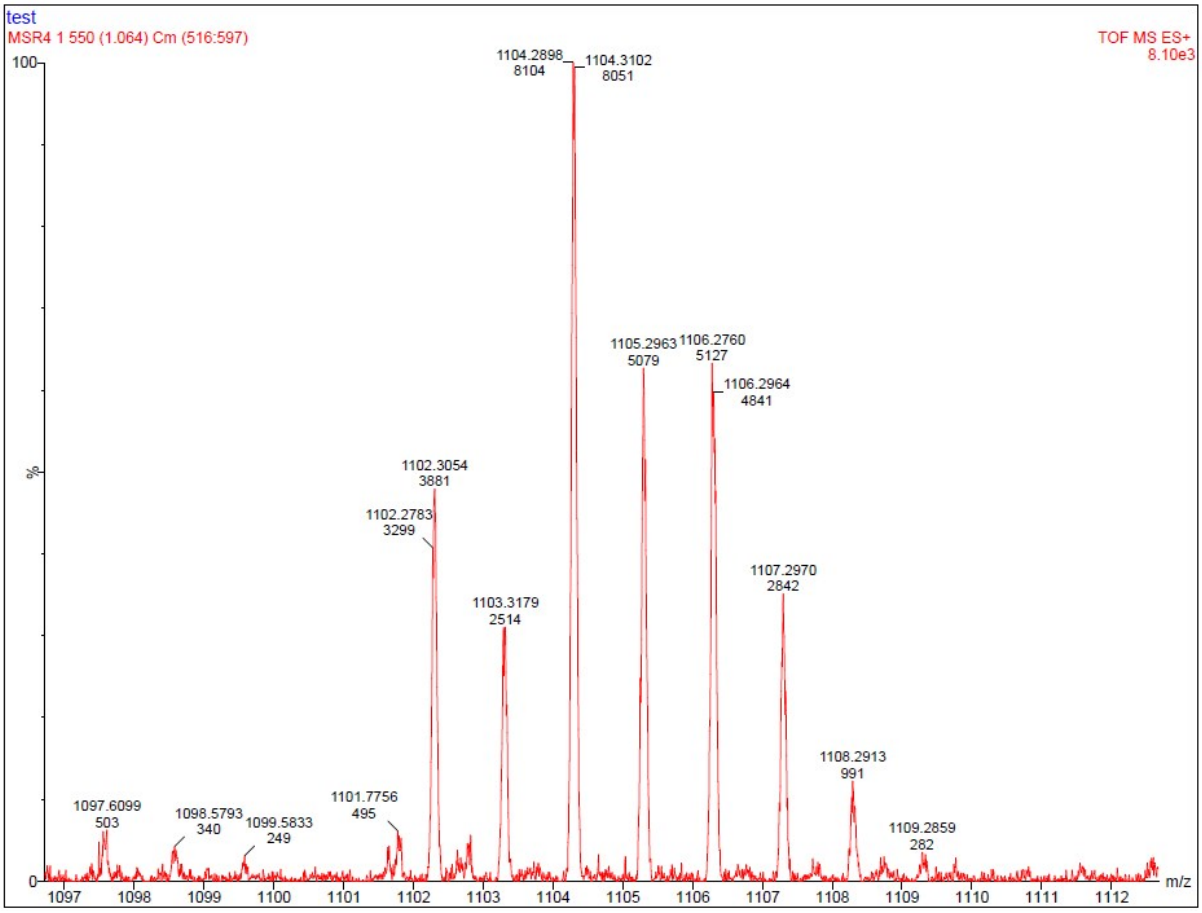

Fig.10. Direct Infusion Electrospray ionization mass spectrum of co-pillar[4+1]arene **3** in chloroform. *m/z* calculated for $C_{59}H_{76}O_{10}Br_2$ $[M+H]^+$: 1104.38; found: 1104.2898 along with other isotopes 1102.3054, 1103.3179,1105.2963, 1106.2760, 1107.2970 and 1108.2913. (*Chem. Commun.,* 2020,**56**, 1792-1794).

S6 Chromatographic separation resolution calculations on silica-bound co-pillar[4+1]arene and RP-C18 HPLC stationary phase.

Chromatographic data and peaks table on silica-bound co-pillar[4+1]arene stationary phase						
Peptides	Retention time (min)	Peak area	Start time (min)	End time (min)	Width at base (min)	Width at 50% (min)
IGNEQGVSR	4.27	32675	3.83	4.71	0.87	0.23
SAEGLDASASLR	4.99	44967	4.64	6.00	1.36	0.22
AVGANPEQLTR	5.48	87843	5.10	6.55	1.45	0.26
VGNEIQYVALR	5.94	145069	5.46	7.29	1.83	0.28
VFTPLEVDVAK	7.94	23811	7.23	8.67	1.44	0.48

Table S1. Chromatographic data and peaks table on silica-bound co-pillar[4+1]arene stationary phase.

Chromatographic data and peaks table on RP-C18 stationary phase						
Peptides	Retention time (min)	Peak area	Start time (min)	End time (min)	Width at base (min)	Width at 50% (min)
IGNEQGVSR	9.43	77773	9.28	9.65	0.37	0.12
AVGANPEQLTR	10.29	224733	10.20	10.42	0.22	0.04
SAEGLDASASLR	10.31	139460	10.24	10.43	0.19	0.04
VGNEIQYVALR	10.37	848562	10.29	10.73	0.44	0.04
VFTPLEVDVAK	10.39	199718	10.31	10.47	0.28	0.08

Table S2. Chromatographic data and peaks table on RP-C18 stationary phase.

S6.1 Chromatographic separation resolution data

The peak width at 50% (FWHM) and retention times of 5 peptides were substituted in the resolution equation to calculate the resolution of 5 peptides on silica bound co-pillar[4+1]arene stationary phase and RP-C18 stationary phase.[3]

$$\text{Resolution R} = 1.18 \times \left[\frac{tr_2 - tr_1}{w0.5_{h1} + w0.5_{h2}}\right]$$

Peptides comparison	Resolution of Chromatogram	
	co-pillar[4+1]arene stationary phase	RP-C18 stationary phase
IGNEQGVSR and VFTPLEVDVAK	6.09	5.66
SAEGLDASASLR & AVGANPEQLTR	1.20	0.29
SAEGLDASASLR & VGNEIQYVAL	2.24	0.88
AVGANPEQLTR & VGNEIQYVALR	1.26	1.32

Table S3. Chromatographic separation resolution of peptide standards on co-pillar[4+1]arene stationary phase and RP-C18 stationary phase.

S6.2 Peak asymmetry data

The peak asymmetry [4] of chromatographic peaks on co-pillar[4+1]arene stationary phase and RP-C18 stationary phase was calculated according to Sciex recommended formula as the experiment was carried out using Analyst® Software provided by Sciex.

$$\text{Peak asymmetry } (A_s) = \left[\frac{peak\ end\ time - retention\ time}{retention\ time - peak\ start\ time}\right]_{=} \frac{b}{a}$$

Peak Asymmetry Data

Silica-bound co-pillar[4+1]arene stationary phase			RP-C18 stationary phase		
IGNEQGVSR	=[4.71-4.27/4.27-3.83]	=1.00	IGNEQGVSR	=[9.65-9.43/9.43-9.28]	=1.46
SAEGLDASASLR	=[6.00-4.99/4.99-4.64]	=2.88	AVGANPEQLTR	=[10.42-10.29/10.29-10.20]	=1.44
AVGANPEQLTR	=[6.55-5.48/5.48-5.10]	=2.81	SAEGLDASASLR	=[10.43-10.31/10.31-10.24]	=2.00
VGNEIQYVALR	=[7.29-5.94/5.94-5.46]	=2.81	VGNEIQYVALR	=[10.73-10.37/10.37-10.29]	=4.50
VFTPLEVDVAK	=[8.67-7.94/7.94-7.23]	=1.02	VFTPLEVDVAK	=[10.47-10.39/10.39-10.31]	=1.00

Table S4. Chromatographic peak asymmetry on co-pillar[4+1]arene stationary phase and RP-C18 stationary phase.

S6 3 Peak tailing data

The peak tailing of chromatographic peaks on co-pillar[4+1]arene stationary phase and RP-C18 stationary phase was calculated according to the following formula.

$$\text{Peak tailing} = \frac{(a+b)}{2a}$$

Peak Tailing Data

Silica-bound co-pillar[4+1]arene stationary phase			RP-C18 stationary phase		
IGNEQGVSR	=[0.44+0.44/2*0.44]	=1.00	IGNEQGVSR	=[0.15+0.22/2*0.15]	=1.23
SAEGLDASASLR	=[0.35+1.01/2*0.35]	=1.94	SAEGLDASASLR	=[0.09+0.13/2*0.09]	=1.22
AVGANPEQLTR	=[0.38+1.07/2*0.35]	=1.92	AVGANPEQLTR	=[0.06+0.12/2*0.06]	=1.50
VGNEIQYVALR	=[0.48+1.35/2*0.48]	=1.90	VGNEIQYVALR	=[0.08+0.36/2*0.08]	=2.75
VFTPLEVDVAK	=[0.71+0.73/2*0.73]	=0.99	VFTPLEVDVAK	=[0.08+0.08/2*0.08]	=1.00

Table S5. Chromatographic peak tailing on co-pillar[4+1]arene stationary phase and RP-C18 stationary phase.

S7 References

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2. M. A. Addicoat and G. F. Metha, J. Comput. Chem., 2009, **30**, 57-64.
3. "About Resolution, Part 1 : SHIMADZU (Shimadzu Corporation)", can be found under https://www.shimadzu.com/an/hplc/support/lib/lctalk/resol-1.html, 2020.
4. "How Is Peak Asymmetry Caluclated in Analyst® Software Quantitate Mode?", can be found under https://sciex.com/support/knowledge-base-articles/how-peak-asymmetry-value-caluclated-in-analyst-quant-mode, 2020.