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® Initiator 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(TM) NanoLC 425 coupled with Sciex Triple-TOF(TM) 5600 mass spectrometer. LC-MS/MS data processed by PeakView(TM) 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.

| Conformer | IGNEQGVR | SAEGLDASL | AVGANPEQL | VGNEIQV | VFTPLEDV |
|-----------|----------|-----------|-----------|---------|----------|
| Gas       | Solvent  | Gas       | Solvent   | Gas     | Solvent  |
| Energy (Hartree) | Energy (Hartree) | Energy (Hartree) | Energy (Hartree) | Energy (Hartree) |
| 1 Blue     | -172.770 | -173.650  | -212.428  | -213.372 | -207.330 |
|           | -172.370 | -173.399  | -207.342  | -208.274 | -208.275 |
|           | -172.415 | -213.396  | -207.364  | -208.287 | -208.296 |
|           | -224.843 | -225.739  | -224.843  | -225.733 | -225.699 |
|           | -216.483 | -217.424  | -216.483  | -217.424 | -217.436 |
| 2 Orange   | -172.791 | -173.682  | -212.370  | -213.339 | -207.342 |
|           | -172.370 | -213.399  | -207.342  | -208.274 | -208.275 |
|           | -172.415 | -213.396  | -207.364  | -208.287 | -208.296 |
|           | -224.843 | -225.733  | -224.843  | -225.733 | -225.699 |
|           | -216.483 | -217.424  | -216.483  | -217.424 | -217.436 |
| 3 Green    | -172.827 | -173.686  | -212.415  | -213.396 | -207.364 |
|           | -172.370 | -213.399  | -207.342  | -208.274 | -208.275 |
|           | -172.415 | -213.396  | -207.364  | -208.287 | -208.296 |
|           | -224.843 | -225.733  | -224.843  | -225.733 | -225.699 |
|           | -216.604 | -217.454  | -216.604  | -217.454 | -217.424 |
| 4 Red      | -172.855 | -173.686  | -212.428  | -213.374 | -207.335 |
|           | -172.370 | -213.399  | -207.342  | -208.274 | -208.275 |
|           | -172.415 | -213.396  | -207.364  | -208.287 | -208.296 |
|           | -224.843 | -225.733  | -224.843  | -225.733 | -225.699 |
|           | -216.604 | -217.454  | -216.604  | -217.454 | -217.424 |
| 5 Yellow   | -172.827 | -173.676  | -212.424  | -213.36  | - |
|           | -172.370 | -213.399  | -207.342  | -208.275 | - |
|           | -172.415 | -213.396  | -207.364  | -208.287 | - |
|           | -224.843 | -225.733  | -224.843  | -225.733 | - |
|           | -216.604 | -217.454  | -216.604  | -217.454 | - |

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 reoptimised 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 the same level of theory as in the gas phase. The gas and solvent phase optimised energies of these complexes, which are presented in Table 3 and 4 respectively, were used to compute the peptides\[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 IGNEQGVS\[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         | -301.878722     | Kick14         | -301.834537   | Kick71         | -301.786777   |
| Kick49        | -301.796223     | Kick51         | -301.811777  | 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           | -301.878652     | 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         | -301.80401   | 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         | -301.781814     | 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 SAEGLDASASL RIP[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      | Kx13            | -341.321653   | Kx13            |
| Kiick25        | -341.40722      | Kx12            | -341.368592   | Kx12            |
| Kiick27        | -341.40559      | Kx19            | -341.367664   | Kk8             |
| Kiick23        | -341.40006      | Kx11            | -341.366046   | Kk10            |
| Kiick24        | -341.39842      | Kx18            | -341.365137   | Kk6             |
| Kiick38        | -341.395745     | Kx15            | -341.364631   | Kk10            |
| Kiick44        | -341.39411      | Kx17            | -341.363246   | Kk30            |
| Kiick45        | -341.392498     | Kx19            | -341.361835   | Kk20            |
| Kiick40        | -341.392484     | Kx28            | -341.361458   | Kk7             |
| Kiick48        | -341.391307     | Kx29            | -341.360072   | Kk3             |
| Kiick41        | -341.390436     | Kx22            | -341.357758   | Kk5             |
| Kiick50        | -341.389976     | Kx23            | -341.357135   | Kk14            |
| Kiick39        | -341.389575     | Kx3             | -341.357135   | Kk22            |
| Kiick34        | -341.389097     | Kx1             | -341.357135   | Kk14            |
| Kiick49        | -341.388526     | Kx4             | -341.356093   | Kk12            |
| Kiick11        | -341.388314     | Kx29            | -341.356603   | Kk16            |
| Kiick13        | -341.385334     | Kx11            | -341.354999   | Kk18            |
| Kiick17        | -341.382992     | Kx1             | -341.354826   | Kk27            |
| Kiick10        | -341.382516     | Kx10            | -341.353393   | Kk22            |
| Kiick34        | -341.382263     | Kx20            | -341.353393   | Kk22            |

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Table 3c: Gas phase energies (Hartree) of AVGANPEQLTRpillar[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 \( \square \text{pillar}[4+1]\text{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 |
| Kick39| -353.763295          | Kick29           | -353.792332     | Kick9  | -353.803601 |
| Kick40| -353.763036          | Kick19           | -353.791373     | Kick18 | -353.801614 |
| Kick37| -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          | Kick11           | -353.787001     | Kick14 | -353.792321 |
| 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 VFTPLEVDVAKpillar[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 |
| Kick24        | -345.454154     | Kick21          | -345.57   |
| Kick25        | -345.45382      | Kick29          | -345.565199 |
| Kick22        | -345.451724     | Kick22          | -345.564127 |
| Kick5         | -345.45117      | Kick7           | -345.563999 |
| Kick4         | -345.449417     | Kick23          | -345.562538 |
| Kick35        | -345.446933     | Kick27          | -345.562178 |
| Kick21        | -345.44661      | Kick30          | -345.562013 |
| Kick26        | -345.446285     | Kick6           | -345.558077 |
| Kick27        | -345.444387     | Kick24          | -345.556307 |
| Kick39        | -345.443392     | Kick20          | -345.555984 |
| Kick23        | -345.443082     | Kick5           | -345.555899 |

Kick52         | -345.565175     |
Kick8          | -345.564356     |
Kick10         | -345.563801     |
Kick9          | -345.56348      |
Kick7          | -345.563477     |
Kick6          | -345.563195     |
Kick51         | -345.562963     |
Kick5          | -345.561439     |
Kick40         | -345.561384     |
Kick39         | -345.561248     |
Kick4          | -345.560175     |
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 IGNEQGVSRpillar[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          | Kick23          | Kick23          | Kick39          | -302.838047     |
| Kick37        | 302.836664      | Kick22         | -302.835526  | Kick21          | Kick25          | Kick25          | Kick51          | -302.827873     |
| Kick38        | 302.835398      | Kick11         | -302.835135  | Kick22          | Kick24          | Kick24          | Kick53          | -302.827869     |
| Kick50        | 302.830568      | Kick38         | -302.83297   | Kick19          | Kick5           | Kick5           | Kick50          | -302.827868     |
| Kick49        | 302.830151      | Kick61         | -302.830598  | Kick23          | Kick3           | Kick3           | Kick47          | -302.827865     |
| Kick48        | 302.826747      | Kick23         | -302.830065  | Kick17          | Kick21          | Kick21          | Kick46          | -302.826648     |
| Kick35        | 302.824172      | Kick46         | -302.828635  | Kick14          | Kick20          | Kick20          | Kick13          | -302.820072     |
| Kick47        | 302.823253      | Kick45         | -302.828616  | Kick28          | Kick15          | Kick15          | Kick20          | -302.818411     |
| Kick13        | 302.819436      | Kick51         | -302.827942  | Kick3           | Kick18          | Kick18          | Kick67          | -302.815973     |
| Kick43        | 302.818425      | Kick49         | -302.827231  | Kick7           | Kick28          | Kick28          | Kick68          | -302.81595      |
| Kick39        | 302.817816      | Kick7          | -302.826102  | Kick25          | Kick16          | Kick16          | Kick66          | -302.815948     |
| Kick40        | 302.817691      | Kick28         | -302.824929  | Kick31          | Kick2           | Kick2           | Kick71          | -302.815253     |
Table 4b: Solvent phase energies (Hartree) of SAEGLDASASLRpillar[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) |
|----------------|------------------|-----------------|--------------|-----------------|
| Kick48         | -342.531522      | Kick112         | -342.490259  | Kick31          | -342.548968     | Kick9          | -342.530586   | Kick8          | -342.520956   |
| Kick45         | -342.531186      | Kick13          | -342.489818  | Kick13          | -342.54863      | Kick29         | -342.529751   | Kick12         | -342.51619    |
| Kick50         | -342.531019      | Kick24          | -342.487327  | Kick12          | -342.548017     | Kick10         | -342.529421   | Kick9          | -342.515739   |
| Kick49         | -342.529595      | Kick25          | -342.487118  | Kick10          | -342.545718     | Kick6          | -342.52701    | Kick14         | -342.512612   |
| Kick44         | -342.529518      | Kick21          | -342.487014  | Kick11          | -342.545039     | Kick16         | -342.525597   | Kick5          | -342.51083    |
| Kick39         | -342.527625      | Kick19          | -342.486558  | Kick29          | -342.544102     | Kick7          | -342.523977   | Kick24         | -342.509731   |
| Kick38         | -342.527284      | Kick30          | -342.486315  | Kick3           | -342.540702     | Kick8          | -342.520755   | Kick21         | -342.508878   |
| Kick40         | -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   |
| Kick27 | -342.524381 | Kick22 | -342.485367 | Kick19 | -342.537477 | Kick11 | -342.51883 | Kick7 | -342.507024 |
|--------|-------------|--------|-------------|--------|-------------|--------|-------------|-------|-------------|
| Kick26 | -342.524342 | Kick4  | -342.484705 | Kick30 | -342.536272 | Kick12 | -342.518285 | Kick20 | -342.506758 |
| Kick25 | -342.524324 | Kick2  | -342.484537 | Kick28 | -342.535543 | Kick22 | -342.516861 | Kick13 | -342.505782 |
| Kick24 | -342.523713 | Kick17 | -342.484325 | Kick18 | -342.535469 | Kick23 | -342.515287 | Kick26 | -342.501597 |
| Kick41 | -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 |
| Kick34 | -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 |

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Table 4c: Solvent phase energies (Hartree) of AVGANPEQL[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 |
| Kick11         | -337.41838       | Kick17        | -337.401346 |
| Kick7          | -337.41777       | Kick14        | -337.397189 |
| Kick8          | -337.41755       | Kick16        | -337.396109 |
| Kick10         | -337.41583       | Kick23        | -337.395476 |
| Kick27         | -337.41466       | Kick15        | -337.394267 |
| Kick9          | -337.41407       | Kick12        | -337.392064 |
| Kick26         | -337.41399       | Kick11        | -337.390578 |
| Kick28         | -337.41311       | Kick5         | -337.390316 |
| Kick5          | -337.4103        | Kick7         | -337.38968  |
| Kick15         | -337.40977       | Kick4         | -337.389623 |
| Kick17         | -337.40893       | Kick20        | -337.389232 |
| Kick16         | -337.40847       | Kick22        | -337.388805 |
| Kick19         | -337.4083        | Kick3         | -337.388496 |
| Kick25         | -337.4079        | Kick6         | -337.386769 |
| Kick18         | -337.40674       | Kick19        | -337.384823 |
| Kick24         | -337.40637       | Kick21        | -337.382387 |
| Kick14         | -337.40483       | Kick2         | -337.382327 |
| Kick3          | -337.40441       | Kick13        | -337.380877 |
| Kick4          | -337.40429       | Kick1         | -337.377402 |
|               |                  | Kick6         | -337.403353 |
Table 4d: Solvent phase energies (Hartree) of VGNEIQYVALRpillar[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 |
| Kick24         | -354.83378       | Kick13          | -354.87389 | Kick11 | -354.874717 |
| Kick24         | -354.83303       | Kick15          | -354.87214 | Kick18 | -354.874144 |
| Kick24         | -354.83182       | Kick11          | -354.87105 | Kick17 | -354.873733 |
| Kick24         | -354.83039       | Kick12          | -354.86906 | Kick8  | -354.872439 |
| Kick24         | -354.82956       | Kick29          | -354.86338 | Kick5  | -354.871574 |
| Kick24         | -354.82781       | Kick18          | -354.86282 | Kick33 | -354.871426 |
| Kick24         | -354.82662       | Kick19          | -354.86059 | Kick2  | -354.871394 |
| Kick  | Value  | Kick  | Value  | Kick  | Value  |
|-------|--------|-------|--------|-------|--------|
| 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 VFTPLEVDVAKpillar[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       | -346.60532      | -346.610601 |
| Kick34        | -346.6185       | -346.60421      | -346.60946 |
| Kick36        | -346.6179       | -346.60171      | -346.607973 |
| Kick39        | -346.6094       | -346.6014       | -346.605214 |
| Kick24        | -346.6072       | -346.59551      | -346.605042 |
| Kick38        | -346.6064       | -346.5876       | -346.604783 |
| Kick25        | -346.6053       | -346.58103      | -346.604547 |
| Kick6         | -346.6051       | -346.58025      | -346.60413 |
| Kick22        | -346.6041       | -346.57979      | -346.603811 |
| Kick26        | -346.6036       | -346.57905      | -346.603737 |
| Kick27        | -346.6023       | -346.57872      | -346.603624 |
| Kick21        | -346.6017       | -346.57635      | -346.602931 |
| Kick5         | -346.6014       | -346.57473      | -346.602881 |
| Kick19        | -346.6011       | -346.57459      | -346.601627 |
| Kick23        | -346.6008       | -346.57378      | -346.601445 |
| Kick4         | -346.6005       | -346.57364      | -346.601026 |
| Kick3         | -346.5947       | -346.56978      | -346.600766 |
| Kick13        | -346.5924       | -346.5664       | -346.600217 |
| Kick2         | -346.5911       | -346.56435      | -346.598358 |
| Kick14        | -346.5868       | -346.56354      | -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 lowest energy conformers of IGNEQGVSR[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides   | Cavity | D (Å) | Peptides   | Cavity | D (Å) | Peptides   | Cavity | D (Å) | Peptides   | Cavity | D (Å) |
|------------|--------|-------|------------|--------|-------|------------|--------|-------|------------|--------|-------|
| C_38-H_53  | C_192  | 2.905 | C_26-H_23  | N_220  | 2.843 | C_26-H_24  | N_218  | 2.822 | C_79-H_84  | N_194  | 2.632 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_08-H_14  | O_172  | 2.250 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 | C_06-H_13  | O_172  | 2.834 |
| C_38-H_53  | O_196  | 2.873 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 | C_37-C_36  | O_223  | 2.953 |

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Table 5b: Gas phase interatomic bond distances between peptide and cavity for lowest energy conformers of SAEGLDASASLR pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.
| Bond         | Distance | Bond         | Distance | Bond         | Distance | Bond         | Distance | Bond         | Distance |
|--------------|----------|--------------|----------|--------------|----------|--------------|----------|--------------|----------|
| C_{137}-C_{133} | 2.857    | C_{137}-C_{133} | 2.797    | C_{137}-C_{133} | 2.819    | C_{137}-C_{133} | 2.552    | C_{137}-C_{133} | 2.74     |
| C_{131}-H_{132} | 2.175    | C_{131}-H_{132} | 2.487    | C_{131}-H_{132} | 2.424    | C_{131}-H_{132} | 2.575    | C_{131}-H_{132} | 2.285    |
| C_{134}-C_{131} | 2.43     | C_{134}-C_{131} | 2.716    | C_{134}-C_{131} | 2.715    | C_{134}-C_{131} | 2.577    | C_{134}-C_{131} | 2.126    |
| N_{129}-H_{130} | 1.533    | N_{129}-H_{130} | 1.513    | N_{129}-H_{130} | 1.528    | N_{129}-H_{130} | 1.578    | N_{129}-H_{130} | 1.578    |
| O_{138}        | 2.675    | O_{138}        | 2.675    | O_{138}        | 2.675    | O_{138}        | 2.675    | O_{138}        | 2.675    |
| C_{134}        | 2.872    | C_{134}        | 2.872    | C_{134}        | 2.872    | C_{134}        | 2.872    | C_{134}        | 2.872    |
| C_{137}        | 2.175    | C_{137}        | 2.175    | C_{137}        | 2.175    | C_{137}        | 2.175    | C_{137}        | 2.175    |

Table 5c: Gas phase interatomic bond distances between peptide and cavity for lower energy conformers of AVGANPEQLTR \pmb{pillar[4+1]}arene complexes, wherein the color coding represents the different conformers plotted in the main text.
Table 5d: Gas phase interatomic bond distances between peptide and cavity for lowest energy conformers of VGNEIQYVALR pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) |
|----------|--------|--------|----------|--------|--------|----------|--------|--------|
| 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_70-H_82 | N_142  | 2.863  | C_65-H_67 | O_252  | 2.283 |
| C_65-H_67 | C_147  | 2.953  | 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_72-H_73 | C_136  | 2.989  | N_106-H_107 | N_193  | 2.751  | C_71-H_73 | O_242  | 2.793 |
| C_87-H_90 | O_141  | 2.712  | O_150-H_108 | C_135  | 2.98  | C_79-H_82 | O_226  | 2.152 |
| C_102-H_105 | C_150  | 2.882  | N_106-H_109 | C_139  | 2.369  | C_83-H_86 | N_281  | 2.897 |
| O_130-H_108 | O_158  | 1.935  | N_106-H_109 | C_224  | 2.202  | C_87-H_90 | O_272  | 2.857 |
| 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  | 2.988  | 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  | 2.953  | C_116-H_121 | O_271  | 2.934  | C_116-H_121 | O_193  | 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  | 2.942  | C_133-N_131 | C_136  | 2.422 |
| O_158-H_132 | C_157  | 1.940  | 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_136  | 2.528  | C_136-C_133 | O_140  | 2.437  | C_136-C_133 | O_140  | 2.437 |
| C_136-C_133 | N_145  | 2.485  | C_136-C_133 | C_135  | 1.55  | C_136-C_133 | C_136  | 1.536 |

Table 5e: Gas phase interatomic bond distances between peptide and cavity for lowest energy conformers of VFTPLEVDVAK pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.
| Peptides       | Cavity | Bl (Å) | Peptides       | Cavity | Bl (Å) | Peptides       | Cavity | Bl (Å) |
|---------------|--------|--------|---------------|--------|--------|---------------|--------|--------|
| C_65-O_1      | O_270  | 2.818  | C_65-H_67     | O_231  | 2.128  | C_68-O_2      | O_205  | 2.083  |
| C_71-O_9      | O_270  | 2.378  | C_71-H_75     | O_231  | 2.245  | C_71-C_14     | O_205  | 2.668  |
| C_65-H_67     | O_270  | 2.377  | C_71-H_80     | O_204  | 2.378  | C_16-C_15     | O_205  | 2.695  |
| C_71-H_75     | O_268  | 2.601  | O_252-H_107   | C_230  | 1.93   | C_15-H_48     | O_205  | 2.771  |
| C_75-H_78     | N_279  | 2.925  | O_252-H_107   | O_232  | 3.001  | C_57-H_59     | C_201  | 2.756  |
| C_79-H_82     | C_265  | 2.959  | C_128-H_131   | C_230  | 2.222  | C_57-H_50     | O_204  | 2.108  |
| C_79-H_82     | O_269  | 2.152  | N_106-H_109   | O_231  | 2.607  | C_57-H_50     | O_205  | 2.675  |
| C_83-H_84     | C_239  | 2.767  | N_106-H_109   | O_243  | 2.692  | C_61-H_62     | O_204  | 2.606  |
| C_83-H_84     | O_243  | 2.550  | C_128-O_127   | O_232  | 2.764  | C_55-H_57     | O_200  | 2.353  |
| C_102-H_104   | O_259  | 2.447  | C_128-H_127   | O_231  | 2.089  | C_68-H_70     | O_205  | 2.424  |
| C_102-H_105   | C_247  | 2.418  | C_128-H_127   | O_231  | 2.454  | C_128-H_72    | C_214  | 2.988  |
| C_122-H_105   | O_259  | 2.755  | C_129-C_126   | N_144  | 2.676  | C_71-H_73     | O_200  | 2.48   |
| C_135-H_118   | O_152  | 2.608  | C_129-C_126   | N_144  | 2.534  | C_87-H_90     | O_204  | 2.266  |
| C_135-H_118   | O_153  | 2.78   | C_132-C_128   | C_134  | 2.539  | C_102-H_104   | N_206  | 2.791  |
| C_135-H_123   | O_152  | 2.526  | C_132-C_128   | C_135  | 2.538  | C_102-H_105   | O_181  | 2.728  |
| C_136-N_124   | N_144  | 2.819  | N_146-C_129   | N_144  | 1.372  | C_102-H_105   | O_175  | 2.867  |
| C_136-C_126   | N_144  | 2.455  | N_146-C_129   | C_134  | 2.461  | C_110-H_111   | C_230  | 2.659  |
| C_136-C_127   | N_144  | 2.746  | C_128-H_130   | C_135  | 2.739  | C_110-H_111   | C_230  | 2.256  |
| C_132-C_128   | C_134  | 2.516  | C_128-H_131   | C_134  | 2.654  | C_116-H_125   | C_230  | 2.811  |
| C_135-C_128   | C_135  | 2.537  | C_135-C_132   | C_134  | 3.408  | C_116-H_132   | O_153  | 2.829  |
| N_144-C_129   | N_144  | 1.368  | C_135-C_132   | C_135  | 1.607  | C_116-H_123   | O_153  | 2.633  |
| N_144-C_129   | C_146  | 2.511  | C_135-C_132   | C_137  | 2.617  | C_116-H_123   | O_232  | 2.786  |
| C_128-H_130   | C_134  | 2.648  | C_135-C_132   | C_138  | 2.637  | C_126-N_124   | N_144  | 2.784  |
| C_128-H_131   | C_135  | 2.77   | C_135-C_132   | C_134  | 2.819  | C_126-N_124   | O_232  | 2.91   |
| C_135-C_132   | C_134  | 1.407  | C_135-O_133   | N_144  | 2.287  | O_252-H_125   | C_230  | 1.955  |
| C_135-C_132   | C_135  | 1.408  | C_129-O_133   | C_134  | 2.825  | O_252-H_125   | O_232  | 0.999  |
| C_135-C_132   | C_137  | 2.437  | O_252-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  | 2.816  | C_135-C_132   | C_134  | 2.54   |
| C_135-O_133   | N_144  | 2.398  | C_132-C_132   | C_135  | 2.533  |
| C_135-O_133   | C_146  | 2.821  | N_144-C_139   | N_144  | 1.274  |
| C_135-O_133   | C_146  | 2.485  |
| C_135-O_133   | C_134  | 2.667  |
| C_135-O_133   | C_131  | 2.825  |
| C_135-O_133   | C_131  | 2.258  |
| C_135-O_133   | C_131  | 2.683  |
| C_135-O_133   | C_131  | 2.785  |
| C_135-O_133   | C_134  | 1.408  |
| C_135-O_133   | C_135  | 1.408  |
Table 5a: Solvent phase interatomic bond distances between peptide and cavity for lowest energy conformers of IGNEQGVSRpillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides       | BL [Å] | Peptides       | BL [Å] | Peptides       | BL [Å] | Peptides       | BL [Å] | Peptides       | BL [Å] | Peptides       | BL [Å] |
|----------------|--------|----------------|--------|----------------|--------|----------------|--------|----------------|--------|----------------|--------|
| IGNEQGVSR_Blue | C_136  | O_143          | 2.971  | C_137          | O_134  | 2.683          | C_138          | O_134  | 2.683          | C_139          | O_134  |
| IGNEQGVSR_Green| C_136  | O_143          | 2.971  | C_137          | O_134  | 2.683          | C_138          | O_134  | 2.683          | C_139          | O_134  |
| IGNEQGVSR_Orange| C_136 | O_143         | 2.971  | C_137          | O_134  | 2.683          | C_138          | O_134  | 2.683          | C_139          | O_134  |
| IGNEQGVSR_Red  | C_136  | O_143          | 2.971  | C_137          | O_134  | 2.683          | C_138          | O_134  | 2.683          | C_139          | O_134  |
| IGNEQGVSR_Yellow| C_136 | O_143        | 2.971  | C_137          | O_134  | 2.683          | C_138          | O_134  | 2.683          | C_139          | O_134  |
Table 5b: Solvent phase interatomic bond distances between peptide and cavity for lower energy conformers of SAEGLDASASLR □pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) |
|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|
| C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      | C_65-H_87 | 1      |
| 2.50     | 2.16   | 0.99   | 2.49     | 2.90   | 3.10   | 2.51     | 2.47   | 2.10   | 2.49     | 2.90   | 3.10   | 2.51     | 2.47   | 2.10   | 2.49     | 2.90   | 3.10   |
| C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      | C_83-H_88 | 1      |
| 2.32     | 2.32   | 2.32   | 2.32     | 2.32   | 2.32   | 2.32     | 2.32   | 2.32   | 2.32     | 2.32   | 2.32   | 2.32     | 2.32   | 2.32   | 2.32     | 2.32   | 2.32   |
| C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 | C_136-H_107 | 1 |
| 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   |
| C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 | C_131-H_132 | 1 |
| 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   |
| C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 | C_137-H_133 | 1 |
| 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   | 2.48     | 2.48   | 2.48   |

SAEGLDASALR_Blue
SAEGLDASALR_Green
SAEGLDASALR_Orange
SAEGLDASALR_Red
SAEGLDASALR_Yellow
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Table 5c: Solvent phase interatomic bond distances between peptide and cavity for lower energy conformers of AVGANPEQLTRpillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) |
|----------|--------|--------|----------|--------|--------|----------|--------|--------|----------|--------|--------|
| AVGANPEQLTR_Blue | C_71-O_4 | 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 |
| AVGANPEQLTR_Green | C_44-C_43 | 2.896 | C_65-H_66 | O_161 | 2.576 | C_83-H_86 | O_220 | 2.48 | C_65-H_66 | O_178 | 2.971 |
| AVGANPEQLTR_Orange | C_32-H_38 | 2.83 | C_120-N_118 | O_266 | 2.893 | C_71-H_72 | N_106-H_109 | 2.294 | N_106-H_109 | O_207 | 2.321 |
| AVGANPEQLTR_Red | C_110-H_111 | 2.925 | C_12-H_93 | O_178 | 2.964 | C_112-H_114 | N_134 | 2.87 | C_120-N_118 | N_208 | 2.999 |

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

| Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) | Peptides | Cavity | BL (Å) |
|----------|--------|--------|----------|--------|--------|----------|--------|--------|
| C_136-O_139 | O_140 | 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 |
| C_136-C_133 | N_145 | 2.467 | O_158-H_132 | O_158 | 0.986 | C_136-C_133 | N_145 | 2.282 |
| O_158-H_132 | O_158 | 0.986 | O_158-H_132 | O_158 | 0.986 | C_136-C_133 | C_133 | 1.556 |
| C_136-C_133 | C_133 | 1.556 | C_136-C_133 | C_136 | 1.502 | C_136-C_133 | C_136 | 2.519 |
| C_136-C_133 | C_136 | 2.519 | C_136-C_133 | O_140 | 2.472 | C_136-C_133 | N_145 | 2.466 |
| C_136-C_133 | O_140 | 2.729 | C_136-C_133 | N_145 | 2.458 | | | |
| 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_133 | 1.556 | C_136-C_133 | C_136 | 1.502 | C_136-C_133 | C_136 | 2.519 |
| C_136-C_133 | C_136 | 2.519 | C_136-C_133 | O_140 | 2.472 | C_136-C_133 | N_145 | 2.466 |
| C_136-C_133 | O_140 | 2.729 | C_136-C_133 | N_145 | 2.458 | | | |
| 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_133 | 1.556 | C_136-C_133 | C_136 | 1.502 | C_136-C_133 | C_136 | 2.519 |
| C_136-C_133 | C_136 | 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 lowest energy conformers of VFTPLEVDVAK [pillar[4+1]arene complexes, wherein the color coding represents the different conformers plotted in the main text.

| Peptides  | Cavity | BL (Å) | Peptides  | Cavity | BL (Å) | Peptides  | Cavity | BL (Å) |
|-----------|--------|--------|-----------|--------|--------|-----------|--------|--------|
| 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 | O_196 | 2.997  |
| C_22-H_100 | O_215 | 2.862  | C_232-H_107 | C_230 | 1.9    | C_102-H_104 | O_200 | 2.688  |
| C_102-H_104 | O_171 | 2.701  | C_232-H_107 | O_232 | 0.995  | C_102-H_105 | O_181 | 2.84   |
| C_102-H_105 | O_171 | 2.69   | C_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   |
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](http://doi.org/10.5281/zenodo.3995081).

S2.5 Specific peptidespillar[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 arginine unit (R) is partially 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 arginine (R) unit is fully inserted into the cavity. | The terminal leucine (L) unit closest to the arginine (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 arginine (R) unit is fully inserted into the cavity. |
| AVGANPEQLTR     | Proline (P) unit               | The threonine                  | The Alanine-                  | Proline (P) unit              | -                              |
| Sequence     | Description                                                                 |
|--------------|-----------------------------------------------------------------------------|
| VGNEIQVALR   | 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) is 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 glutamic 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 5-5 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, SAEGLDASLR, 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 5-5 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, SAEGLDASLR, 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 |
**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 \( \text{C}_{59}\text{H}_{76}\text{O}_{10}\text{Br}_{2} \ [\text{M+H}]^{+} \): 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.

| 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.
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.²

\[
R = 1.18 \times \frac{t_{r2} - t_{r1}}{w_{0.5,h1} + w_{0.5,h2}}
\]

| Peptides   | Resolution of Chromatogram |
|------------|-----------------------------|
| IGNEQGVSR and VFTPLEVDVAK | 6.09 | 5.66 |
| SAEGLDASASLR & AVGANEQQLTR | 1.20 | 0.29 |
| SAEGLDASASLR & VGNEIQYVALR | 2.24 | 0.88 |
| AVGANEQQLTR & 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 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.

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

| Peptides   | Silica-bound co-pillar[4+1]arene stationary phase | RP-C18 stationary phase |
|------------|--------------------------------------------------|-------------------------|
| IGNEQGVSR | [4.71-4.27/4.27-3.83] | IGNEQGVSR = [9.65-9.43/9.43-9.28] | 1.00 | 1.46 |
| SAEGLDASASLR | [6.00-4.99/4.99-4.64] | AVGANEQQLTR = [10.42-10.29/10.29-10.20] | 2.88 | 1.44 |
| AVGANEQQLTR | [6.55-5.48/5.48-5.10] | SAEGLDASASLR = [10.43-10.31/10.31-10.24] | 2.81 | 2.00 |
| VGNEIQYVALR | [7.29-5.94/5.94-5.46] | VGNEIQYVALR = [10.73-10.37/10.37-10.29] | 2.81 | 4.50 |
| VFTPLEVDVAK | [8.67-7.94/7.94-7.23] | VFTPLEVDVAK = [10.47-10.39/10.39-10.31] | 1.02 | 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 | IGNEQGVSR =0.15+0.22/2*0.15 | 1.00 |
| SAEGLDASASLR =0.35+1.01/2*0.35 | SAEGLDASASLR =0.09+0.13/2*0.09 | 1.94 |
| AVGANPEQLTR =0.38+1.07/2*0.35 | AVGANPEQLTR =0.06+0.12/2*0.06 | 1.92 |
| VGNEIQYVALR =0.48+1.35/2*0.48 | VGNEIQYVALR =0.08+0.36/2*0.08 | 1.90 |
| VFTPLEVDVAK =0.71+0.73/2*0.73 | VFTPLEVDVAK =0.08+0.08/2*0.08 | 0.99 |

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

**S7 References**

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