**Supporting Information**

**Supramolecular chromatographic separation of $C_{60}$ and $C_{70}$ fullerenes: flash column chromatography versus high pressure liquid chromatography**

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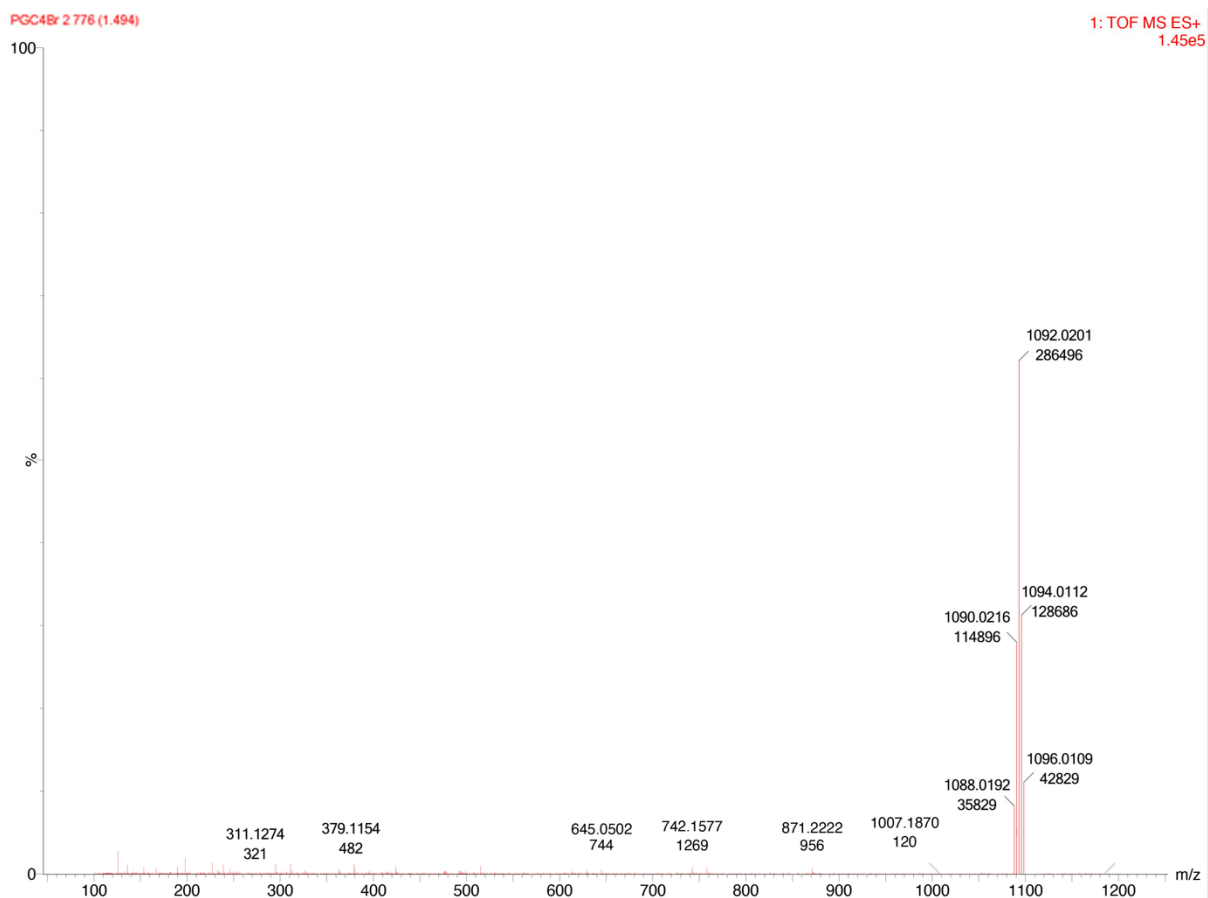**1.** Characterization of C-bromo-butylpyrogallol[4]arene **2**



Figure S1. Mass Spectrum of *C*-bromo-butylpyrogallol[4]arene **2**. ESI-MS *m/z* calculated for $C_{44}H_{52}{}^{79}Br_4O_{12}$ [M]$^+$ was 1088.01, found for [M]$^+$ to [M+8]$^+$ were 1088.0192, 1090.0216, 1092.0201, 1094.0112 and 1096.0109.
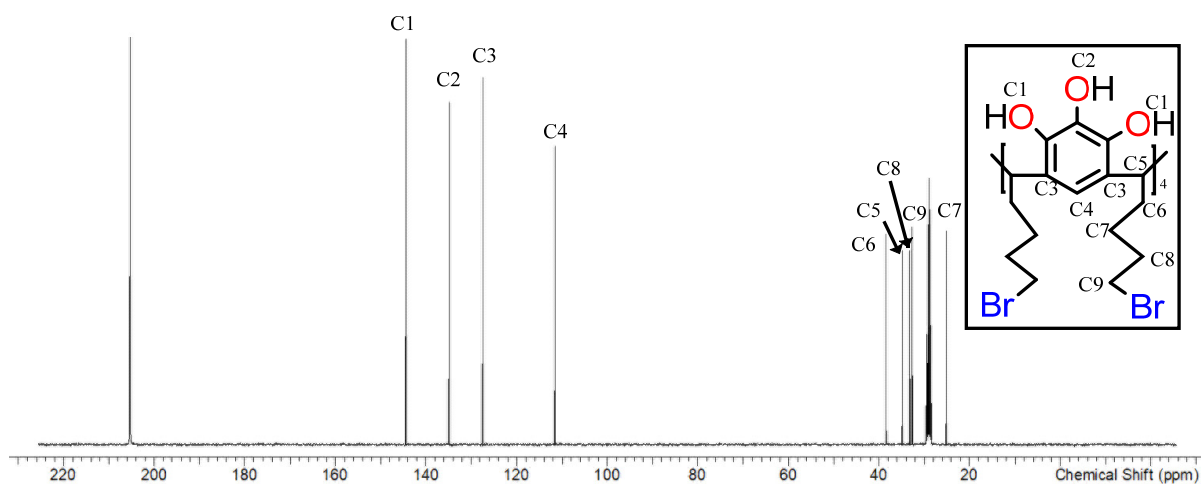


Figure S2. $^{13}$C NMR spectrum (101 MHz, d$_6$-Acetone, room temperature) of *C*-bromo butylpyrogallol[4]arene **2**.

2. Computational data

All the structures, long range interactions and energies of these 20 energy minima can be freely accessed at  http://doi.org/10.5281/zenodo.4147306.

3. Binding energies and modes for $C_{60} \subset RP\text{-}C_{18}$ and $C_{70} \subset RP\text{-}C_{18}$

To gauge the interactions between RP-$C_{18}$ and the fullerenes, a host-guest interaction study was performed to compute the binding energies of $C_{60} \subset RP\text{-}C_{18}$ and $C_{70} \subset RP\text{-}C_{18}$ motifs. This was done using two conformers of RP-$C_{18}$, a straight chain and a curved conformer as input structures. These computations were performed for both the gas and solvent phase using the same level of theory as stated in the main text for the computation of the host-guest interactions of fullerene$\subset C$-butylpyrogallol[4]arene complexes. The computed gas and solvent phase Gibbs free binding energies ($\Delta$GBE) and electronic energies are presented Table S1. The detailed energetic parameters are presented in Table S2 and S3 for the gas and solvent phases respectively.

It can be observed from Table S1 that the interaction energies of $C_{70} \subset RP\text{-}C_{18}$ are much lower (nearer to negative) in comparison to $C_{60} \subset RP\text{-}C_{18}$ both in the gas and solvent phase. This shows a stronger binding affinity of $C_{70}$ to RP-$C_{18}$ in comparison to $C_{60}$, consequently resulting in a preferential selective separation of $C_{70}$ over $C_{60}$.

However, the small positive Gibbs free binding energies for these interactions indicate that the interactions between RP-$C_{18}$ and the fullerenes are significantly weak (thermodynamically unfovorable) and consequently the RP-$C_{18}$ stationary phase is less favourable for the separation of fullerenes in comparison to $C$-butylpyrogallol[4]arene.
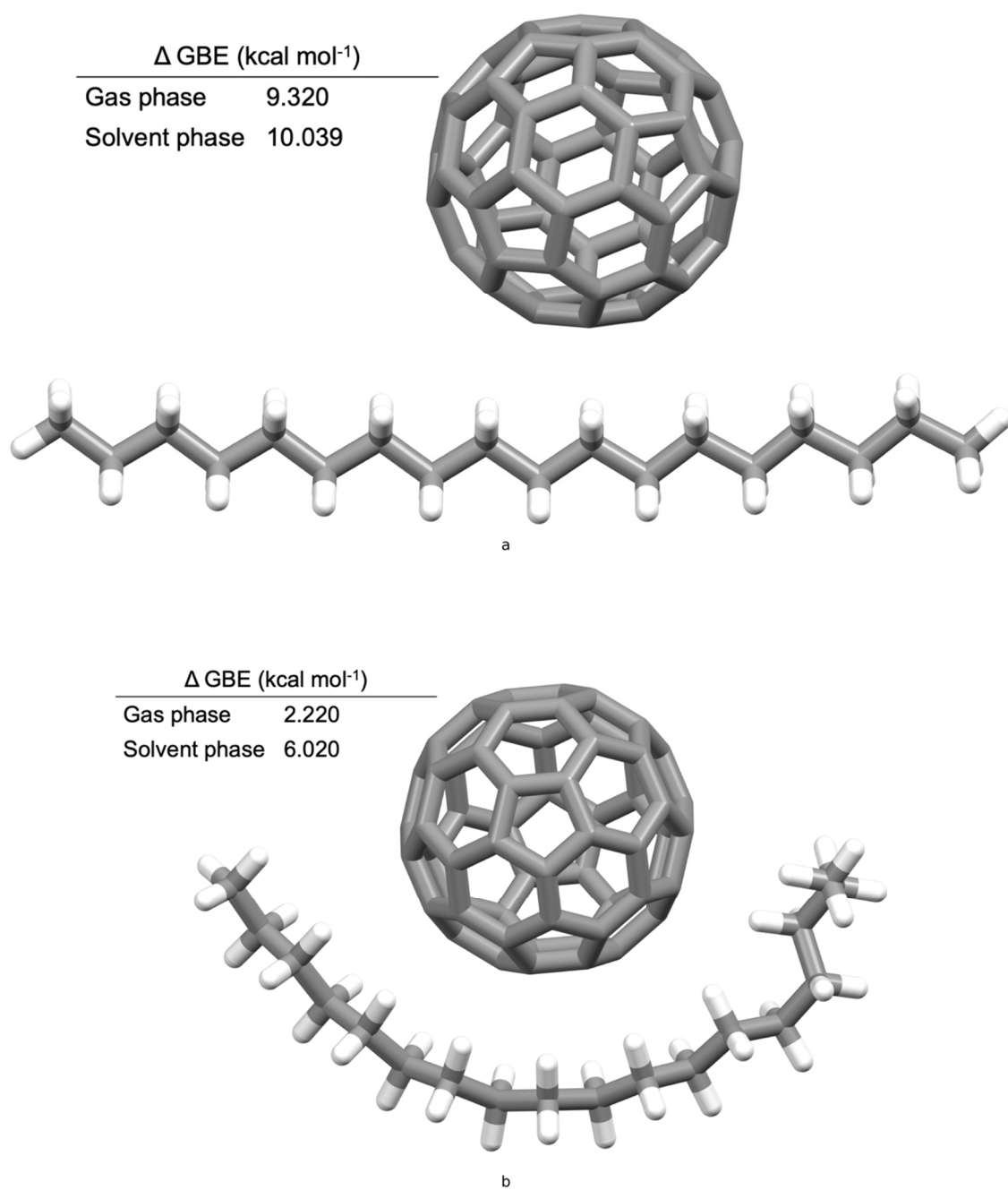
| ΔGBE (kcal mol$^{-1}$) | |
| --- | --- |
| Gas phase | 9.320 |
| Solvent phase | 10.039 |

a

| ΔGBE (kcal mol$^{-1}$) | |
| --- | --- |
| Gas phase | 2.220 |
| Solvent phase | 6.020 |

b

Figure S3: Illustration of the calculated gas and solvent phase binding energies and modes of $C_{60} \subset RP\text{-}C_{18}$ interaction: a) represents the binding mode between the straight chain conformer of RP-$C_{18}$ and $C_{60}$, and b) represents the binding mode between the curved conformer of RP-$C_{18}$ and $C_{60}$.
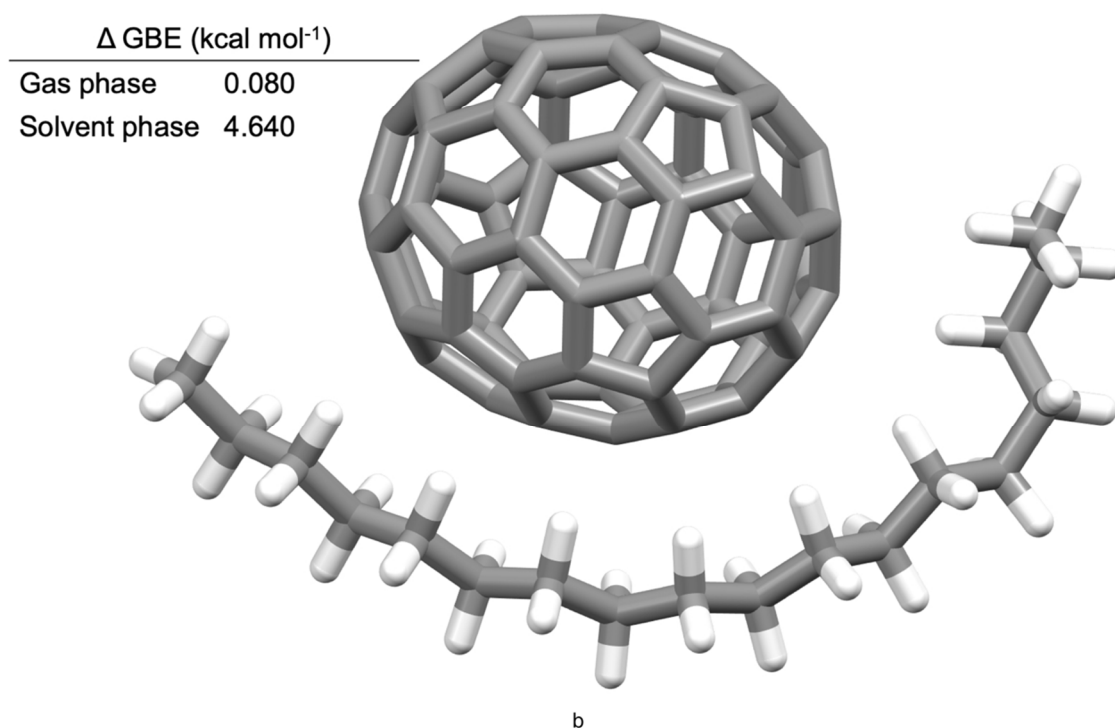
| $\Delta$ GBE (kcal mol$^{-1}$) | |
| --- | --- |
| Gas phase | 0.470 |
| Solvent phase | 4.0478 |

a

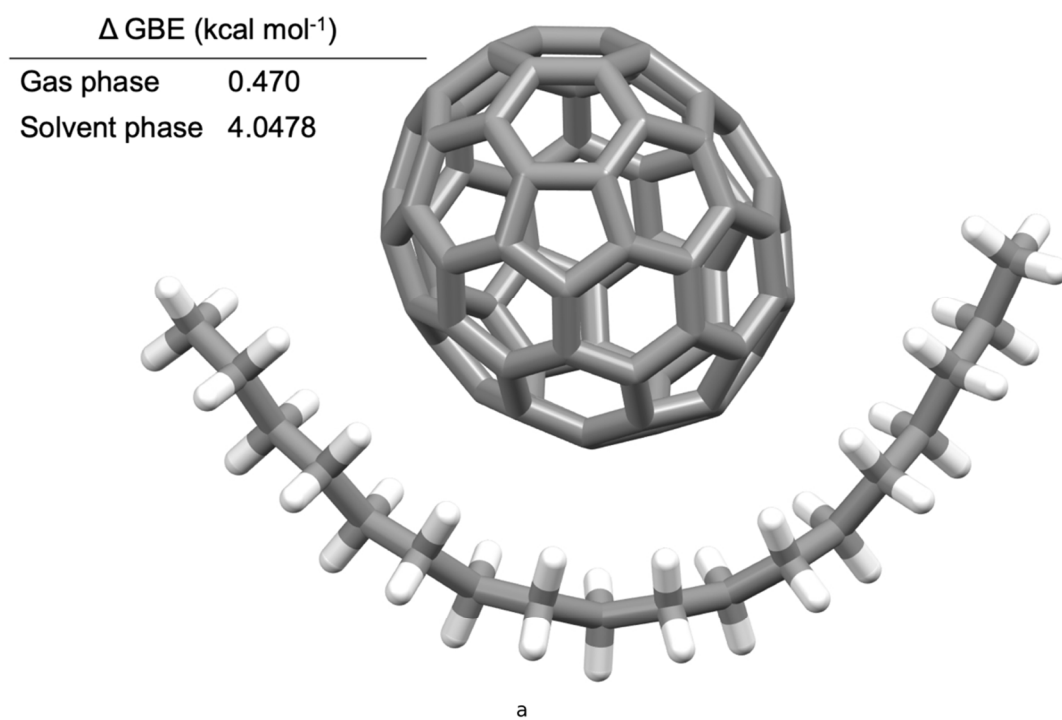| $\Delta$ GBE (kcal mol$^{-1}$) | |
| --- | --- |
| Gas phase | 0.080 |
| Solvent phase | 4.640 |

b

Figure S4: Illustration of the calculated gas and solvent phase binding energies and modes of $C_{70} \subset RP\text{-}C_{18}$. a and b represent the binding mode of two curved conformers of RP-$C_{18}$ with $C_{70}$.

Table S1: Change in electronic energy and Gibbs free binding energy of fullerene⊂RP-C$_{18}$ motifs.

| Systems | Gas phase (kcal mol$^{-1}$) | | Solvent phase (kcal mol$^{-1}$) | |
|---|---|---|---|---|
| | ΔE | ΔGBE | ΔE | ΔGBE |
| C$_{60}$⊂RP-C$_{18}$-a | -0.0153 | 9.320 | -9.478 | 10.039 |
| C$_{60}$⊂RP-C$_{18}$-b | -0.028 | 2.220 | -12.987 | 6.020 |
| C$_{70}$⊂RP-C$_{18}$-a | -0.0311 | 0.470 | -14.315 | 4.0478 |
| C$_{70}$⊂RP-C$_{18}$-b | -0.0307 | 0.080 | -14.301 | 4.640 |

*E* is the electronic change of the system, in practice is the final optimised energy the system. *ΔE* is the change in electronic energy between the complex and the isolated systems.

$$\Delta E = E_{fullerene \subset RP-C_{18}} - (E_{fullerene} - E_{RP-C_{18}})$$

$E_{fullerene \subset RP-C18}$ is the electronic energy of the fullerene⊂RP-C$_{18}$ motif. $E_{fullerene}$ is the electronic energy of the isolated fullerene and E$_{RP-C18}$ is the electronic energy of the isolated RP-C$_{18}$.

GBE is the Gibbs free energy of the system. This was computed as follows:

$$GBE = E + H - TS$$

*H* is the thermal correction to the enthalpy of the system. *S* is the thermal correction to entropy. *T* is the temperature of the system which is equal to 298.15 K.

$$\Delta GBE - GBE_{fullerene \subset RP-C_{18}} - (GBE_{fullerene} - GBE_{RP-C_{18}})$$

$GBE_{fullerene \subset RP-C18}$ is the Gibbs free energy of the fullerene⊂RP-C$_{18}$ motif. $GBE_{fullerene}$ is the Gibbs free energy of the isolated fullerene and G$_{RP-C18}$ is the Gibbs free energy of the isolated RP-C$_{18}$.

Table S2: Gas Phase UFF DFTB Mio-1-1 Contributions the Gibbs Free Energy (Hartree)

| Systems | Electronic energies | RT | -TS | Internal energies | Enthalpies | Gibbs Free energies |
|---|---|---|---|---|---|---|
| $C_{60}$ | -102.6746482 | 0.000944186 | -0.064338271 | -102.2522524 | -102.2513083 | -102.3156465 |
| $C_{70}$ | -119.8820304 | 0.000944186 | -0.070701247 | -119.387666 | -119.3867218 | -119.4574231 |
| RP-$C_{18}$ | -45.10614778 | 0.000944186 | -0.079772362 | -44.55891042 | -44.55796623 | -44.63773859 |
| $C_{60} \subset$RP-$C_{18}$-a | -147.7961452 | 0.000944186 | -0.111769899 | -146.8277065 | -146.8267623 | -146.9385322 |
| $C_{60} \subset$RP-$C_{18}$-b | -147.8088012 | 0.000944186 | -0.111966711 | -146.8388275 | -146.8378833 | -146.9498501 |
| $C_{70} \subset$RP-$C_{18}$-a | -165.0192592 | 0.000944186 | -0.117773367 | -163.9775864 | -163.9766423 | -164.0944156 |
| $C_{70} \subset$RP-$C_{18}$-b | -165.0188829 | 0.000944186 | -0.118983495 | -163.976999 | -163.9760548 | -164.0950383 |

Table S3: Solvent Phase UFF DFTB Mio-1-1 Contributions the Gibbs Free Energy (Hartree)

| Systems | Electronic energies | RT | -TS | Internal energies | Enthalpies | SASA Free Energy | Gibbs Free energies |
|---|---|---|---|---|---|---|---|
| $C_{60}$ | -102.7139323 | 0.000944186 | -0.064366 | -102.291834 | -102.2908898 | -0.03929056 | -102.3552558 |
| $C_{70}$ | -119.9269967 | 0.000944186 | -0.07072882 | -119.4329698 | -119.4320256 | -0.04497303 | -119.5027544 |
| RP-$C_{18}$ | -45.13065122 | 0.000944186 | -0.07933919 | -44.58411324 | -44.58316905 | -0.02453648 | -44.66250824 |
| $C_{60} \subset$RP-$C_{18}$-a | -147.8596879 | 0.000944186 | -0.10955973 | -146.8931503 | -146.8922061 | -0.06372944 | -147.0017658 |
| $C_{60} \subset$RP-$C_{18}$-b | -147.8652793 | 0.000944186 | -0.11301986 | -146.8960955 | -146.8951513 | -0.05785244 | -147.0081712 |
| $C_{70} \subset$RP-$C_{18}$-a | -165.0804601 | 0.000944186 | -0.12000952 | -164.0397467 | -164.0388025 | -0.06170926 | -164.158812 |
| $C_{70} \subset$RP-$C_{18}$-b | -165.080438 | 0.000944186 | -0.1194558 | -164.0393571 | -164.038413 | -0.06209017 | -164.1578688 |