Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

A push-and-pull model for allosteric anion binding in cage complexes: ESI

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1 Electronic structure calculations

All geometry optimizations were carried out at the BP86/def2-SVP level of theory. These include the single $[Pd(Pyr)_4]^{2+}$ complex as well as the structures for BF_4^- between the two planes (which is the only anion with internal degrees of freedom). The latter included 95 atoms in total, so that only small basis DFT calculations were feasible. However, this should not have a large impact in the final results since only the structure of the BF_4^- is relaxed and its orientation should be mostly conditioned by electrostatic interactions. The latter can be adequately reproduced even at a lower level of theory.

In order to compute the potential energy surfaces, density fitted second-order Møller-Plesset perturbation theory (DF-MP2)[1] with the cc-pVTZ basis set (cc-pVTZ-PP for Pd, with the ECP28MDF pseudopotential) was the method of choice.[2, 3] While computing the energy, and since a wide range of distances was explored, it was necessary to correctly model electrostatic, polarization as well as dispersion interactions between the anion and the planes. MP2 theory gives a good compromise between accuracy and computational cost, while avoiding the use of parameterization (such as in dispersion corrected DFT[4]). With the use of density fitting approximations, it can be straightforwardly applied to systems with 100 atoms or more. The density fitting basis sets used were the cc-pVTZ/JKFIT[5] (def2-TZVPP JK-fitting basis in the case of Pd)[6] for the HF calculations, and cc-pVTZ/MP2FIT[7] (def2-TZVPP correlation fitting basis for Pd)[8] in the MP2 correlation part.

2 Potential energy fits

A global fit of 5 Gaussians against the BF_4^-@cage and Cl^-@cage effective interaction potential following Eq.(3) in the paper was carried out. The fit was applied to the total DF-MP2 interaction energy. There was no separation into different interaction terms. As described in the paper, the OGOLEM framework was used for the genetic algorithms

based global optimization. As OGOLEM implements a pool concept instead of the traditional generation-based concept for maintaining the genetic population, a diversity criterion is needed. This diversity criterion helps to avoid premature convergence of the pool by effectively eliminating the possibility for two (or more) identical individuals to enter the pool. As the fitness in case of parameter optimization is based on the total deviations of fitted energies to their corresponding reference, a fitness of 0.0 E_h would correspond to a perfect fit. The diversity criterion specifies the minimal allowed fitness difference between two individuals so that they are considered divers/separate local minima. A value of $1 \cdot 10^{-5}$ E_h was used in all fitting runs.

The final potential and the individual Gaussian contributions can be found in Figs.1 and 2 for BF_4^- and Cl^-, respectively. The red line shows the final fitted potential for each of the systems. The reference data points are also shown. The overall interaction profile is for both cases roughly described with a single gaussian function (shown in light green). In the case of Cl^- there is a second gaussian which is also quite significant to describe the asymmetry around the minimum. The results also show that 3 functions could have sufficed to describe the potential correctly. Given the nature of the algorithm, the inclusion of 2 extra functions leads to no artifacts as the extra functions are automatically set to values close to zero in the region of fitting. In other cases, functions can also cancel out.

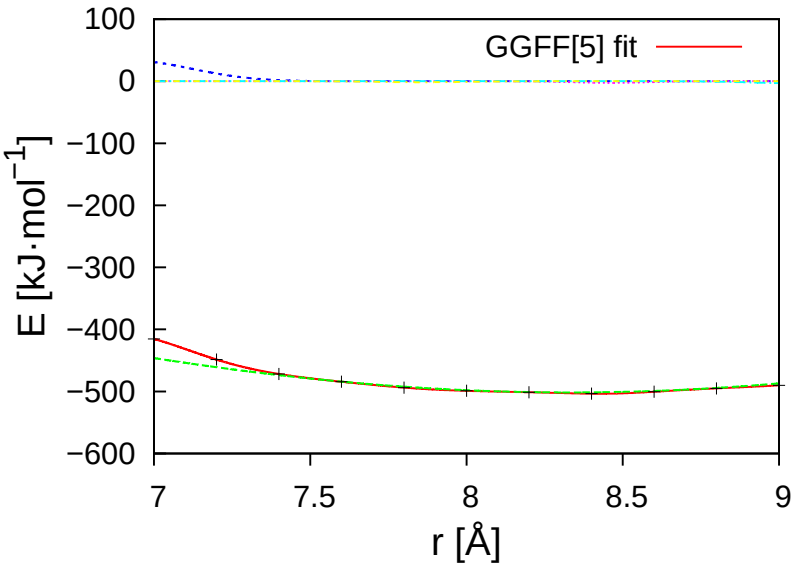

Figure 1: GGFF[5] fit of the BF_4^-@cage interaction energy and single Gaussian contributions.

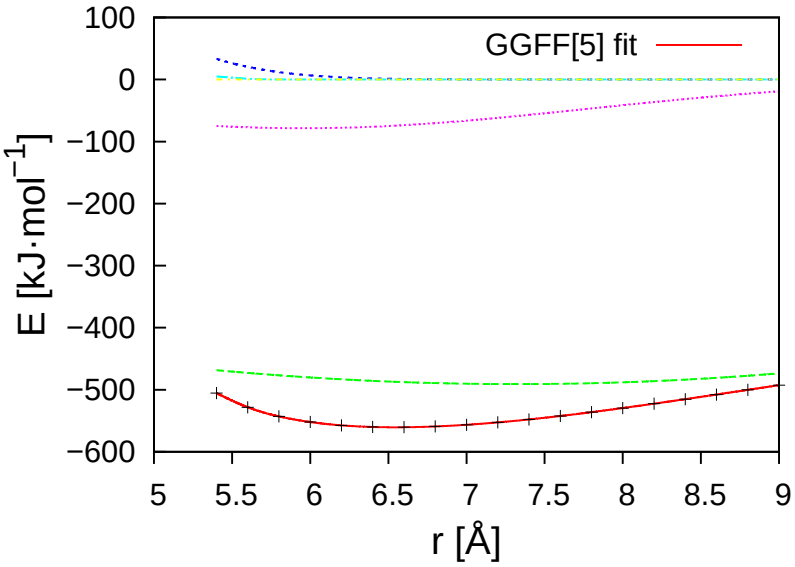

Figure 2: GGFF[5] fit of the Cl^-@cage interaction energy and single Gaussian contributions.

3 Model Structure in xyz-Format

Model structure of Cl^-@cage with $r = 8.0$ Å between the planes in cartesian coordinate format (xyz).

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   91

Pd      0.000000      0.000000      0.000000
 N      0.000000      2.061504      0.000000
 N     -2.061504      0.000000      0.000000
 N      2.061504      0.000000     -0.000000
 N     -0.000000     -2.061504      0.000000
 C      0.480790     -2.748212     -1.070023
 C      0.491938     -4.148040     -1.104720
 C      0.000000     -4.863587     -0.000000
 C     -0.491938     -4.148040      1.104719
 C     -0.480790     -2.748213      1.070023
 C      0.480790      2.748212      1.070023
 C      0.491938      4.148040      1.104720
 C      0.000000      4.863587      0.000000
 C     -0.491938      4.148040     -1.104719
 C     -0.480790      2.748213     -1.070023
 C      2.748212      0.480790     -1.070023
 C      4.148040      0.491938     -1.104720
```

C	4.863587	0.000000	-0.000000
C	4.148040	-0.491938	1.104719
C	2.748213	-0.480790	1.070023
C	-2.748212	-0.480790	-1.070023
C	-4.148040	-0.491938	-1.104720
C	-4.863587	-0.000000	-0.000000
C	-4.148040	0.491938	1.104719
C	-2.748213	0.480790	1.070023
H	0.887382	-4.663225	-1.992873
H	-0.887381	4.663226	-1.992872
H	4.663225	0.887382	-1.992873
H	-4.663225	-0.887382	-1.992873
H	5.964848	0.000000	-0.000000
H	4.663226	-0.887381	1.992872
H	2.153198	-0.865985	1.912258
H	2.153197	0.865985	-1.912259
H	-5.964848	-0.000000	-0.000000
H	-4.663226	0.887381	1.992872
H	-2.153198	0.865985	1.912258
H	-2.153197	-0.865985	-1.912259
H	0.000000	-5.964848	-0.000000
H	-0.887381	-4.663226	1.992872
H	-0.865985	-2.153198	1.912258
H	0.865985	-2.153197	-1.912259
H	0.000000	5.964848	0.000000
H	0.887382	4.663225	1.992873
H	0.865985	2.153197	1.912258
H	-0.865985	2.153198	-1.912258
Pd	0.000000	0.000000	8.000000
N	-0.705076	1.937180	8.000000
N	-1.937180	-0.705076	8.000000
N	1.937180	0.705076	8.000000
N	0.705076	-1.937180	8.000000
C	1.391739	-2.418035	6.929977
C	1.880984	-3.729630	6.895281
C	1.663445	-4.570277	8.000000
C	0.956443	-4.066135	9.104719
C	0.488149	-2.746915	9.070023
C	-0.488149	2.746915	9.070023
C	-0.956442	4.066135	9.104719
C	-1.663445	4.570277	8.000000
C	-1.880984	3.729630	6.895281
C	-1.391739	2.418035	6.929977
C	2.418035	1.391739	6.929977
C	3.729630	1.880984	6.895281
C	4.570277	1.663445	8.000000
C	4.066135	0.956443	9.104719
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C	-4.570277	-1.663445	8.000000
C	-4.066135	-0.956443	9.104719
C	-2.746915	-0.488149	9.070023
H	2.428783	-4.078496	6.007127
H	-2.428783	4.078496	6.007128
H	4.078496	2.428783	6.007127
H	-4.078496	-2.428783	6.007127
H	5.605124	2.040099	8.000000
H	4.685501	0.761051	9.992872
H	2.319528	-0.077323	9.912258
H	1.727159	1.550197	6.087741
H	-5.605124	-2.040099	8.000000
H	-4.685501	-0.761051	9.992872
H	-2.319528	0.077323	9.912258
H	-1.727159	-1.550197	6.087741
H	2.040099	-5.605124	8.000000
H	0.761051	-4.685501	9.992872
H	-0.077323	-2.319528	9.912258
H	1.550197	-1.727159	6.087741
H	-2.040098	5.605124	8.000000
H	-0.761051	4.685500	9.992873
H	0.077323	2.319528	9.912258
H	-1.550197	1.727159	6.087742
Cl	0.000000	0.000000	4.000000

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