Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY MATERIAL

Trapping Ca^+ inside a Molecular Cavity: Computational study of the potential energy surfaces for Ca^+-[n]cycloparaphenylene, n=5-12

Cole D. Allen,[†] Susan L.B. Rempe,[‡*] Timothy S. Zwier[§*] and Pengyu Ren,[†*]

[†]Department of Biomedical Engineering, University of Texas at Austin, Austin, TX 78712 USA

[‡]Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

[§]Sandia National Laboratories, Gas Phase Chemical Physics, Livermore, CA 94550 USA

*Susan B. Rempe, Timothy S. Zwier, Pengyu Ren

Email: slrempe@sandia.gov, tszwier@sandia.gov, pren@utexas.edu

Table S1: Raw QM data for Na^+-Benzene.					
Distance (Å)	SAPT0 (kcal/mol)	SAPT2+ (kcal/mol)	B3LYP (kcal/mol)	B3LYP-GD3BJ (kcal/mol)	wb97X-D (kcal/mol)
2.30	-6.97	-6.90	-9.71	-11.60	-9.12
2.50	-13.65	-13.27	-15.53	-17.35	-15.33
2.70	-18.20	-17.61	-19.39	-21.15	-19.63
2.80	-21.11	-20.37	-21.74	-23.45	-22.41
2.90	-22.78	-21.95	-22.96	-24.66	-24.13
3.20	-23.53	-22.63	-23.36	-25.16	-25.01
3.50	-23.62	-22.66	-23.17	-25.31	-25.24
4.00	-23.24	-22.25	-22.57	-25.28	-25.00
4.50	-19.50	-18.46	-18.39	-23.10	-21.19
5.00	-14.15	-13.25	-13.03	-19.16	-15.09

Table S2: Raw QM data for K^+-Benzene.					
Distance (Å)	SAPT0 (kcal/mol)	SAPT2+ (kcal/mol)	B3LYP (kcal/mol)	B3LYP-GD3BJ (kcal/mol)	wb97X-D (kcal/mol)
2.30	2.21	1.58	1.78	-0.85	-1.08
2.50	-9.74	-9.51	-8.93	-11.34	-11.74
2.70	-15.01	-14.37	-13.51	-15.69	-16.33
2.80	-16.14	-15.38	-14.45	-16.55	-17.28
2.90	-16.63	-15.79	-14.81	-16.91	-17.65
3.20	-15.88	-14.96	-13.99	-17.06	-16.72
3.50	-13.78	-12.90	-12.06	-15.78	-14.43
4.00	-10.14	-9.45	-8.84	-15.09	-10.48
4.50	-7.39	-6.87	-6.44	-10.43	-7.51
5.00	-5.50	-5.10	-4.80	-7.12	-5.48

Table S3: Raw QM data for Ca^+-Benzene.				
Distance (Å)	SAPT0 (kcal/mol)	B3LYP (kcal/mol)	B3LYP-GD3BJ (kcal/mol)	wb97X-D (kcal/mol)
1.90	29.97	39.34	35.57	30.77
2.20	-17.11	-1.55	-5.03	-6.97
2.30	-23.42	-8.91	-12.28	-14.06
2.40	-27.27	-13.85	-17.12	-18.78
2.50	-29.31	-17.00	-20.2	-21.75
2.60	-30.06	-18.83	-22.06	-23.43
3.00	-26.49	-19.06	-26.36	-23.28

3.50	-18.69	-14.39	-22.84	-17.49
4.00	-12.62	-10.00	-15.69	-11.65
4.50	-8.68	-6.94	-10.32	-7.68
5.00	-6.17	-4.98	-6.90	-5.36

Table S4: Raw QM data for binding energy, association energy, ZPE and BSSE correction.

[n]CPP	$E_{complex\ raw}$ (Hartree)	$E_{CPP\ raw}$ (Hartree)	$E_{Ca^+\ raw}$ (Hartree)	$E_{complex\ ZPE}$ (kcal/mol)	$E_{CPP\ ZPE}$ (kcal/mol)	ΔE_{ZPE} (kcal/mol)
[5]CPP	-1832.124289	-1154.738626	-677.294275	254.14	255.04	-0.90
[6]CPP	-2063.117075	-1385.757573		307.38	306.83	0.55
[7]CPP	-2294.116692	-1616.760706		359.09	358.34	0.75
[8]CPP	-2525.120166	-1847.766113		410.45	409.76	0.69
[9]CPP	-2756.113922	-2078.761097		461.98	461.35	0.63
[10]CPP	-2987.111924	-2309.760026		513.25	512.54	0.71
[11]CPP	-3218.102377	-2540.751156		564.82	564.19	0.62
[12]CPP	-3449.092763	-2771.741565		616.23	615.55	0.68
[5]CPP flat	-1371.486903	-694.142642		167.42	166.62	0.79
[3]CPP flat	-1833.460006	-1156.113401		270.06	269.28	0.80
Ca^+-Bz	-909.503474	-232.171992		64.57	63.82	0.75
Ca^+-[8]CPP Outside	-2525.113767	-1847.766113		410.39	409.76	0.63

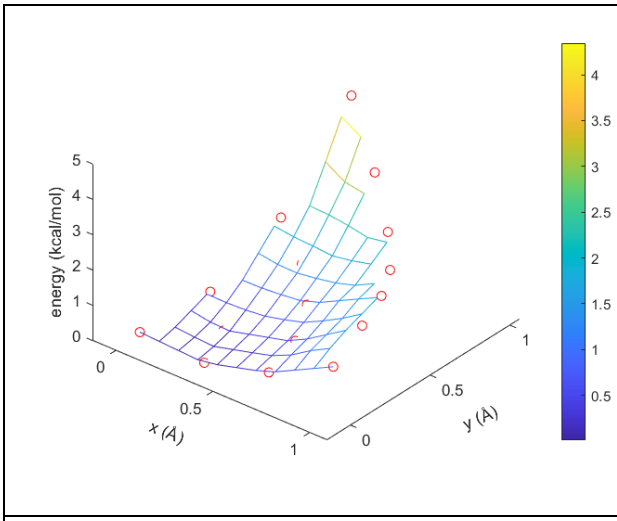
Table S4 (cont.)

[n]CPP	$\Delta E_{Asso\ raw}$ (kcal/mol)	$\Delta E_{BSSE\ raw}$ (Hartree)	ΔE_{BSSE} (kcal/mol)	$\Delta E_{BSSE\ corected\ Asso\ raw}$ (kcal/mol)	ΔE_{Asso} (kcal/mol)	ΔE_{Bind} (kcal/mol)
[5]CPP	-68.08	0.002329	1.46	-66.62	-67.52	-56.79
[6]CPP	-42.21	0.001669	1.05	-41.16	-40.61	-39.33
[7]CPP	-40.20	0.001594	1.00	-39.20	-38.45	-36.97
[8]CPP	-38.89	0.001489	0.93	-37.96	-37.27	-35.89
[9]CPP	-38.06	0.001367	0.85	-37.21	-36.58	-35.26
[10]CPP	-37.44	0.001354	0.85	-36.59	-35.88	-34.60
[11]CPP	-36.94	0.001301	0.82	-36.12	-35.49	-34.29
[12]CPP	-36.77	0.001254	0.79	-35.98	-35.30	-34.25
[5]CPP flat	-31.88	0.001186	0.75	-31.13	-31.89	-31.26
[3]CPP flat	-33.47	0.001252	0.79	-32.68	-30.33	-29.82
Ca^+-Bz	-23.78	0.000569	0.35	-23.43	-22.68	-22.25
Ca^+-[8]CPP Outside	-34.25	0.001379	0.87	-33.38	-32.75	-32.00

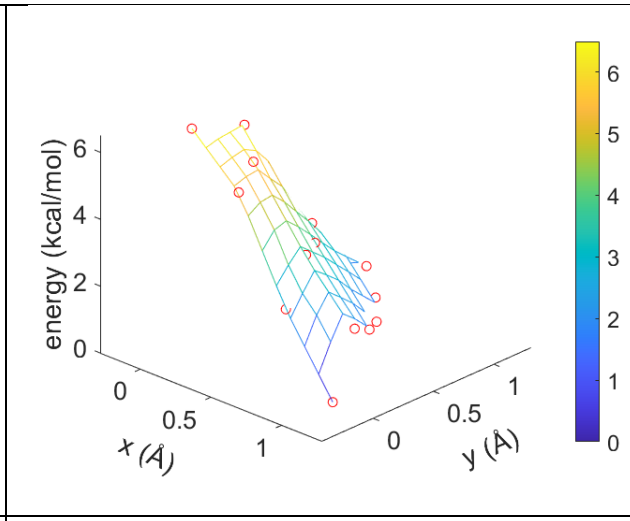
Table S5: PES data plotted for Ca^{+}-[8]CPP.		
X (Å)	Y (Å)	Relative Energy (kcal/mol)
0.00	0.00	20.63
1.28	0.00	13.92
1.18	0.49	13.52
0.90	0.90	12.75
2.75	0.00	0.41
2.70	0.54	0.36
2.54	1.05	0.27
2.29	1.53	0.22
1.95	1.95	0.28
2.05	0.00	4.97
2.01	0.40	4.90
1.89	0.78	4.72
1.70	1.14	4.43
1.45	1.45	4.20
2.40	0.00	1.87
2.35	0.47	1.86
2.22	0.92	1.72
2.00	1.33	1.60
1.70	1.70	1.57
3.00	0.00	1.08
2.94	0.58	0.64
2.77	1.15	0.14
2.49	1.67	0.00
2.12	2.12	0.19
3.25	0.00	3.61
3.19	0.63	2.31
3.00	1.24	0.86
2.70	1.81	0.05
2.30	2.30	0.03
3.50	0.00	8.09
3.43	0.68	6.36
3.23	1.34	5.82
2.91	1.94	6.25
2.47	2.47	8.09

Table S6: Raw PES QM data for Ca^+-[8]CPP. r (red) and Θ (blue) (shown in figure 4) were used for ion placement.

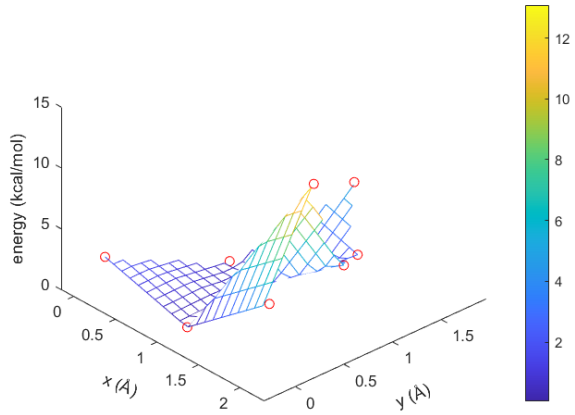
r (Å)	Θ (degrees)	Θ (radians)	$E_{PES\ point\ raw}$ (Hartree)	Relative Energy (kcal/mol)
0.00	0.00	0.00	-2525.086237	20.63
1.28	0.00	0.00	-2525.096930	13.92
1.28	22.50	0.39	-2525.097568	13.52
1.28	45.00	0.79	-2525.098808	12.75
2.75	0.00	0.00	-2525.118464	0.41
2.75	11.25	0.20	-2525.118541	0.36
2.75	22.50	0.39	-2525.118684	0.27
2.75	33.75	0.59	-2525.118767	0.22
2.75	45.00	0.79	-2525.118670	0.28
2.05	0.00	0.00	-2525.111200	4.97
2.05	11.25	0.20	-2525.111310	4.90
2.05	22.50	0.39	-2525.111593	4.72
2.05	33.75	0.59	-2525.112062	4.43
2.05	45.00	0.79	-2525.112433	4.20
2.40	0.00	0.00	-2525.116137	1.87
2.40	11.25	0.20	-2525.116162	1.86
2.40	22.50	0.39	-2525.116372	1.72
2.40	33.75	0.59	-2525.116564	1.60
2.40	45.00	0.79	-2525.116623	1.57
3.00	0.00	0.00	-2525.117396	1.08
3.00	11.25	0.20	-2525.118105	0.64
3.00	22.50	0.39	-2525.118900	0.14
3.00	33.75	0.59	-2525.119119	0.00
3.00	45.00	0.79	-2525.118834	0.18
3.25	0.00	0.00	-2525.113370	3.61
3.25	11.25	0.20	-2525.115437	2.31
3.25	22.50	0.39	-2525.117747	0.86
3.25	33.75	0.59	-2525.119038	0.05
3.25	45.00	0.79	-2525.119077	0.03
3.50	0.00	0.00	-2525.106229	8.09
3.50	11.25	0.20	-2525.108978	6.25
3.50	22.50	0.39	-2525.109851	5.82
3.50	33.75	0.59	-2525.109152	6.25
3.50	45.00	0.79	-2525.106229	8.09



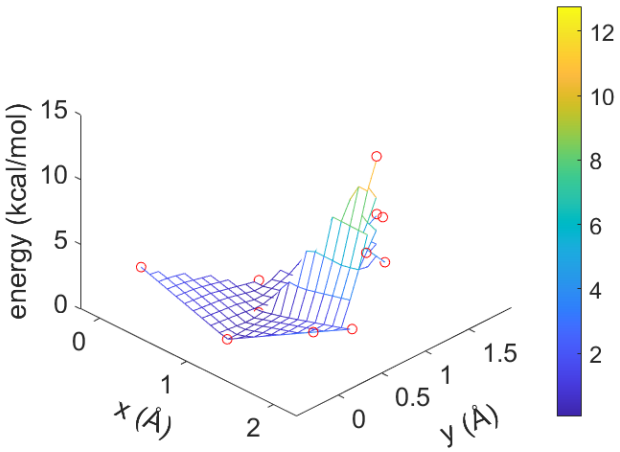
Rigid [5]CPP-Ca⁺ Slice



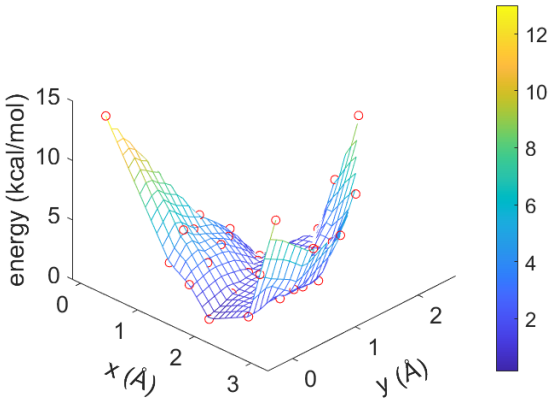
Relaxed [5]CPP-Ca⁺ Slice



Rigid [6]CPP-Ca⁺ Slice

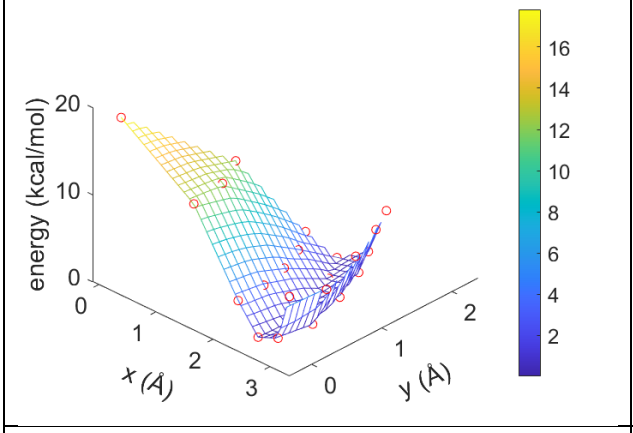


Relaxed [6]CPP-Ca⁺ Slice

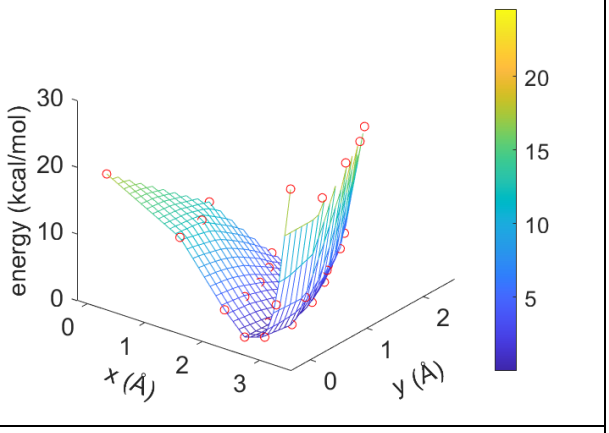


Relaxed [7]CPP-Ca⁺ Slice

Figure S1: Rigid potential energy surface for 'slices' of Ca^+-[n]CPP (n=5-6) complexes and relaxed potential energy surface for a 'slice' of Ca^+-[n]CPP (n=7) using wb97XD/6-31+G(d). Each red circle represents a location the ion was placed at. All energy values are relative to the globale minimum.

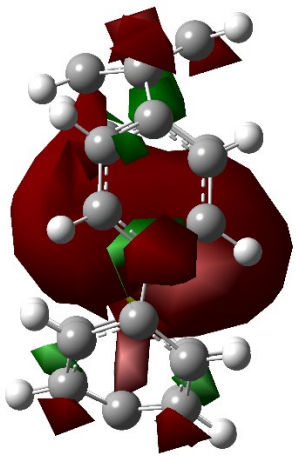


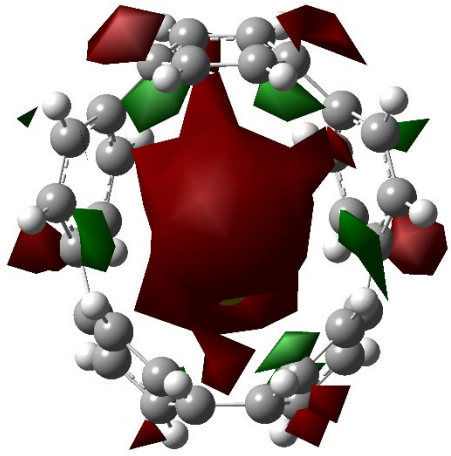
Rigid [8]CPP-Ca^+ Slice



Relaxed [8]CPP-Ca^+ Slice with Rigid Outer Points

Figure S2: Rigid potential energy surface for 'slices' of Ca^+-[n]CPP (n=8) complexes and relaxed potential energy surface for a 'slice' of Ca^+-[n]CPP (n=8) with large outer wall from sp/rigid points using wb97XD/6-31+G(d). Each red circle represents a location the ion was placed at. All energy values are relative to the globale minimum.





[5]CPP LUMO

Figure S3: Lowest unoccupied molecular orbitals (LUMO) for Ca^+-[5]CPP complex. Side (left) and frontal (right) views are shown to describe the distorted s orbital of the Ca^+. LUMO is shown to characterize the Ca^+ s orbital.

The following can be found on https://github.com/prenlab/ioncavity : benzene-ion input/output files, optimization/frequency/rigidPES/relaxedPES input/output files (for each CPP), BSSE/Counterpoise input/output files (for each CPP) total PES data sets from **tables S5** and **S6** (for each CPP), PES interactable MATLAB figures