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GIAO-DFT calculated and experimentally derived complexation-induced chemical shifts of calix[4]arene–solvent inclusion complexes †

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Various possible geometries of host–guest complexes of *p-tert*-butylcalix[4]arene with guest molecules such as toluene or THF are modeled using fast force field optimisations. Based on minima structures obtained by this approach quantum chemical gauge-independent atomic orbital (GIAO)-DFT NMR calculations [B3LYP/3-21G and B3LYP/6-31G(d)] were performed. By a comparison of the theoretically derived chemical shifts for the guest molecule in the host–guest complex with the chemical shifts calculated for the free guest using the same theoretical approach, calculation of complexation-induced chemical shifts (CISs) is possible. Spatial arrangements for which the theoretically derived complexation-induced shifts are in accordance with data stemming from CP-MAS ^{13}C NMR spectroscopy also show reasonable agreement with structures obtained by single crystal structure determinations. Thus, it is possible for calix[4]arene complexes using a combination of force field geometry optimisation and GIAO-DFT NMR shift calculations to screen various starting geometries against experimental data yielding good structural models for these complexes in the solid state.

Introduction

Supramolecular chemistry strongly depends on the three-dimensional arrangement of the corresponding building blocks. Therefore, good structural models of supramolecular assemblies such as host–guest complexes are crucial to understand why and how the "superstructure" is formed, and which intermolecular forces are involved in the formation process. Calix[*n*]arenes are an interesting class of compounds which can enclose cations, anions and uncharged guest molecules to yield such supramolecular structures.[1–5] A key step in the investigation of such complexes is the determination of the spatial arrangement of the aggregate. For the solid-state, single-crystal X-ray structure determination[6] is regarded as the ultimate structural proof. However, this methodology strongly depends on the accessibility of single-crystalline material. In cases where such crystalline material is not available, ^{13}C CP-MAS NMR,[7–16] vibrational spectroscopy,[17–24] or thermochemical methods[25–28] are applicable. In solution, NMR titration experiments have found widespread use for the characterisation of inclusion processes.[1,2,29,30] By comparing the chemical shifts of selected nuclei of the free host or guest molecule, respectively, with the host–guest assembly, complexation-induced changes in the chemical shifts (CIS) can be used to develop three-dimensional structural models. These CIS values are usually interpreted only qualitatively on the bases of "chemical intuition" or results obtained by molecular modeling.[31]

For quantitative approaches the estimation of chemical shifts based on classical descriptions of the aromatic ring current and linear electric field effects for various calculated geometries of a host–guest complex can be applied.[30–32] A good agreement of experimentally derived and calculated NMR data were found for force field calculated models of the complexes having similar geometries to X-ray crystal structures. This approach, however, lacks general applicability because the model for the ring current depends on the host and has to be adapted for different host structures.

In contrast, GIAO-DFT NMR calculations[33–36] are independent of such model assumptions and can be used for any host–guest system and for both ^{1}H and ^{13}C NMR chemical shifts.[32,37–39]

Because small geometrical displacements of the considered atoms have large effects on the chemical shifts, NMR shift calculations are highly dependent on the quality of the geometry used.[31] For the *p-tert*-butylcalix[4]arene–CS_2 inclusion complex (**1**–**2**) theoretically derived CIS values at the GIAO-DFT (B3LYP)/6-311G(d,p)//RHF/6-31G(d) level of theory are in good agreement with experimentally observed values obtained by solid-state NMR spectroscopy ($CIS_{calc} = -1.1$ ppm, $CIS_{exp} = -2.2$ ppm).[40] However, high-level geometry optimizations require essentially more computer time than the chemical shift calculation.[38,40] Thus alternative methods are necessary if large, non-symmetrical molecular assemblies are the focus of attention. Forsyth and Sebag[41] have shown for a series of 38 small organic compounds that the ^{13}C NMR chemical shifts estimated by *ab initio* GIAO-DFT NMR calculations based on force field (MMX or MM3) geometries are in good agreement (rms error 2–4 ppm) with the experimentally observed shifts. Similar errors could be found for estimations based on high level geometry optimizations, *i.e.* the B3LYP/6-31G(d) level of theory. Therefore, a combination of the calculation of magnetic properties at the *ab initio* level using geometries optimized with force field methods is a promising approach for the comparison of experimentally observed and theoretically derived NMR data[38,41] of large systems.

Herein, we report a comparison of *ab initio* calculated and experimentally determined solid-state ^{13}C NMR chemical shifts of inclusion complexes of *p-tert*-butylcalix[4]arene (**1**) with

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† Electronic supplementary information (ESI) available: calculated and observed NMR data and geometrical details for complexes **1**–**3**, **1**–**4** and **1**–**5**. See http://www.rsc.org/suppdata/p2/b1/b110078p/

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Table 1 Selected ^{13}C CP-MAS NMR data of *p-tert*-butylcalix[4]arene–solvent complexes **1**–**2**, **1**–**3**, **1**–**4**, and **1**–**5**[26]

Entry	Guest	Complex		δ_C (ppm)		
				Solid	Solution	$\Delta\delta_C{}^a$(ppm)
1	CS_2	**1–2**	$\mathit{C}S_2$	190.1	192.3	−2.2
2	Toluene	**1–3**	Ph–$\mathit{C}H_3$	15.2	21.4	−6.2
3	THF	**1–4**	$CH_2\mathit{C}H_2O$	67.5	67.7	−0.2
				66.8	67.7	−0.9
			$\mathit{C}H_2CH_2O$	24.2	25.5	−1.3
				23.7	25.5	−1.8
4	Acetone	**1–5**	$Me_2\mathit{C}$=O	201.9	206.5	−4.6
			$H_3\mathit{C}$–CO	27.5	29.8	−2.3

[a] CIS = Complexation-induced chemical shift of the guest: $\Delta\delta = \delta$(solid state) − δ(solution).

various solvent molecules, namely CS_2 (**2**), toluene (**3**), THF (**4**), and acetone (**5**) which have been characterized recently by solid-state ^{13}C NMR spectroscopy and by thermogravimetric analysis (TGA).[26]

Results and discussion

p-tert-Butylcalix[4]arene–solvent complexes were prepared easily by recrystallisation of the macrocyclic host molecule from the corresponding solvent.[26] Selected ^{13}C CP-MAS NMR data of these complexes are summarized in Table 1 together with the derived complexation-induced chemical shifts (CIS) observed for various guest molecules.

Due to the high symmetry (C_4) of the *p-tert*-butylcalix[4]-arene–carbon disulfide complex (**1**–**2**), as shown by the crystal structure,[17] this host–guest system was chosen for model studies. Based on the experimentally derived crystal structure, the complexation-induced chemical shift of the guest was calculated at various levels of theory. In all cases (Table 2, entries 1–3) the upfield shift of the central carbon atom of the CS_2-guest is described correctly by the calculations, although overestimated. Basis set super-positioning errors[42,43] are neglected as is dynamical behavior in the supramolecular assembly. Because of the deep inclusion (>90%) of the guest in the cavity of the calix[4]arene host, medium or packing effects on the chemical shift calculations do not play a role either. The property calculations for the gas phase describe the experimental data at least qualitatively. *Ab initio* optimization of the host–guest structure at the HF/6-31G(d) level of theory, using the crystal structure as a starting geometry, resulted in reduction of symmetry from the initial C_4 symmetry to C_2 symmetry. Furthermore, the entrapment of the CS_2-guest was underestimated by the HF optimization process (Fig. 1); the inclusion of carbon disulfide subsides from 92% observed in the crystal lattice to 57% for the calculated structure.[40] Accordingly, the calculated CIS value of −1.10 ppm, based on the HF optimized structure (Table 2, entry 4), is lower compared to the previously discussed values (Table 2, entries 1–3), but is still in good agreement with the experimentally observed CIS of −2.2 ppm.

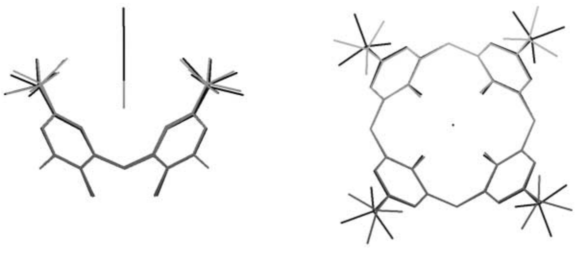


Fig. 1 Overlay of the structures of the *p-tert*-butylcalix[4]arene–CS_2 complex 1–**2** obtained by single crystal structure determination[17] (gray) *ab initio* geometry optimization (HF/6-31G(d); black); hydrogen atoms are omitted for clarity; left: side view, right: top view.

Table 2 GIAO-DFT calculated and experimentally derived CIS[a] for the central carbon atom of the guest in the *p-tert*-butylcalix[4]arene–CS_2 complex (**1**–**2**)

Entry		$\Delta\delta_C{}^a$(ppm)
1	B3LYP/3-21G//experimental geometry	−4.28
2	B3LYP/6-31G(d)//experimental geometry	−4.69
3	B3LYP/6-31G(d,p)//experimental geometry	−3.63
4	B3LYP/6-311G(d,p)//HF/6-31G(d)	−1.10
5	Experiment	−2.20

[a] CIS = Complexation-induced chemical shift of the guest: $\Delta\delta = \delta$(solid state) − δ(solution).

Owing to the large number of atoms in the investigated complexes, high-level *ab initio* optimizations are very expensive in terms of CPU time. However, single point GIAO-DFT NMR calculations require only 10–20% of the CPU time used for the optimizations. Therefore, an alternative method was tested to evaluate the geometries and magnetic properties of *p-tert*-butylcalix[4]arene complexes with toluene (**1**–**3**), THF (**1**–**4**), and acetone (**1**–**5**), for which ^{13}C CP-MAS NMR data have been published previously.[26] Based on Merck94 force field (MMFF) optimized structures, GIAO-DFT NMR shift calculations (B3LYP/3-21G or B3LYP/6-31G(d)) were performed. Fig. 2 shows a correlation of the experimental ^{13}C chemical shifts of toluene, THF, and acetone in solution compared with data obtained from calculations with the MMFF optimized structures. The excellent linear correlation (R^2 > 0.999) proves the applicability of this approach as already confirmed by similar calculations based on the MMX or MM3 force field.[44] Various starting geometries of the host–guest complexes describing rational spatial arrangements of host and guest were subjected to MMFF optimizations usually yielding minimum structures (Fig. 3) with similar potential energies. Based on these structures NMR calculations were performed and CIS for

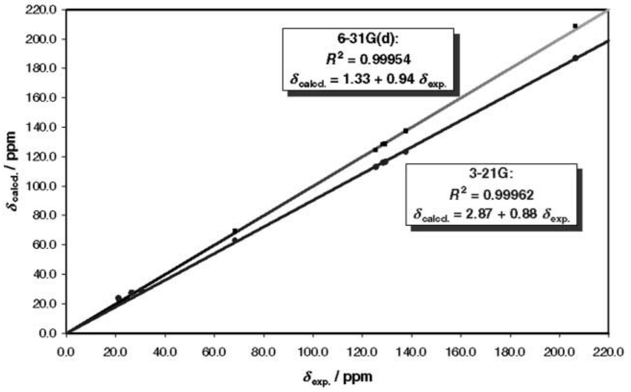


Fig. 2 Correlation of GIAO-DFT calculated (B3LYP/3-21G//MMFF, B3LYP/6-31G(d)//MMFF) with experimentally observed ^{13}C NMR chemical shifts for toluene (**3**), THF (**4**) and acetone (**5**).

Table 3 GIAO-DFT calculated and experimentally derived CIS[a] of toluene in the *p-tert*-butylcalix[4]arene–toluene complex (**1**–**3**)

	Δδ_C[a](ppm)			
Geometry	**(1–3)A**	**(1–3)B**	**(1–3)C**	Exp.
E_{rel}[b]	0.0	0.2	5.1	—
Ph–*C*H$_3$[c]	−3.65	−0.34	−0.02	−6.2
	−4.47	*−0.07*	*−0.57*	

[a] Δδ denotes an upfield shift of the ^{13}C NMR signal of the observed carbon atom. [b] Potential energy (kcal mol^{-1}) obtained from the force field (MMFF) optimization. [c] First line GIAO-DFT(B3LYP)/3-21G//MMFF, second line (italics) GIAO-DFT(B3LYP)/6-31G(d)//MMFF.

Table 4 GIAO-DFT calculated and experimentally derived CIS[a] of THF in the *p-tert*-butylcalix[4]arene–THF complex (**1**–**4**)

	Δδ_C[a](ppm)			
Geometry	**(1–4)A**	**(1–4)B**	**(1–4)C**	Exp.
E_{rel}[b]	0.9	0.0	0.3	—
*C*H$_2$O[c]	−1.56	−0.04	−0.68	−0.9
	−1.46	*−0.15*	*−0.69*	
*C*H$_2$O	0.11	−0.78	−0.27	−0.2
	0.21	*−0.75*	*−0.18*	
*C*H$_2$CH$_2$	−1.03	−2.46	−1.93	−1.3
	−0.52	*−2.70*	*−1.75*	
*C*H$_2$CH$_2$	−2.14	−0.41	−2.79	−1.8
	−2.34	*−0.01*	*−2.99*	

[a] Δδ denotes an upfield shift of the ^{13}C NMR signal of the observed carbon atom. [b] Potential energy (kcal mol^{-1}) obtained from the force field (MMFF) optimization. [c] First line GIAO-DFT(B3LYP)/3-21G//MMFF, second line (italics) GIAO-DFT(B3LYP)/6-31G(d)//MMFF.

Table 5 GIAO-DFT calculated and experimentally derived CIS[a] of acetone in the *p-tert*-butylcalix[4]arene–acetone complex (**1**–**5**)

	Δδ_C[a](ppm)			
Geometry	**(1–5)A**	**(1–5)B**	**(1–5)C**	Exp.
E_{rel}[b]	0.0	8.6	0.0	—
H$_3$*C*–CO[c]	−2.21	−0.24	2.85	−2.3
	−2.51	0.65	3.55	
H$_3$*C*–CO	2.71	−0.24	−1.56	−2.3
	3.55	0.64	*−1.64*	
C=O	6.03	−4.22	6.08	−4.6
	5.52	*−2.07*	5.51	

[a] Δδ denotes an upfield shift of the ^{13}C NMR signal of the observed carbon atom. [b] Potential energy (kcal mol^{-1}) obtained from the force field (MMFF) optimization. [c] First line GIAO-DFT(B3LYP)/3-21G//MMFF, second line (italics) GIAO-DFT(B3LYP)/6-31G(d)//MMFF.

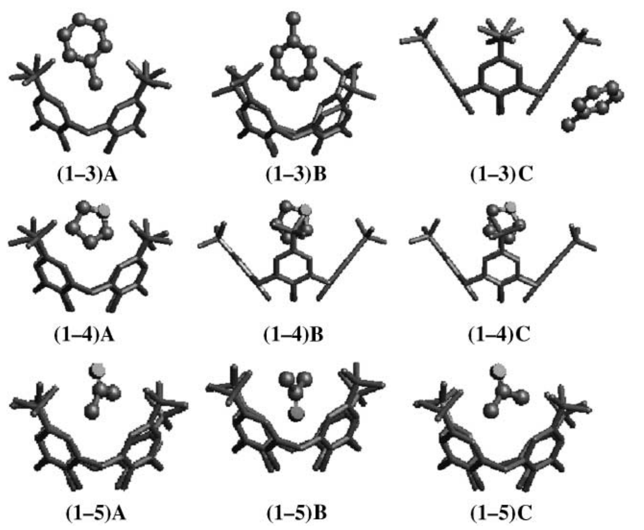


Fig. 3 MMFF optimized structures of *p-tert*-butylcalix[4]arene complexes with toluene (**1**–**3**), THF (**1**–**4**) acetone (**1**–**5**) (for computational details see text); hydrogen atoms are omitted for clarity.

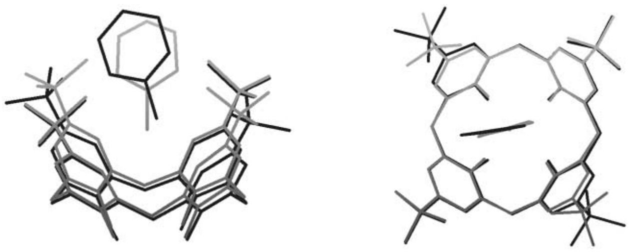
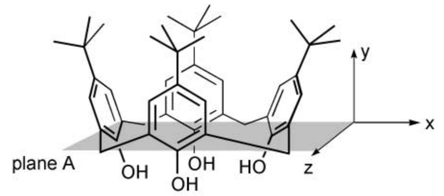


Fig. 4 Overlay of the structures of the *p-tert*-butylcalix[4]arene–toluene complex obtained by single crystal structure determination[45] (gray) MMFF geometry optimization (black; **(1–3)A**); hydrogen atoms are omitted for clarity; left: side view, right: top view.

the included guest molecules are deduced. The results of the calculations are summarized in Tables 3–5.

In the case of the *p-tert*-butylcalix[4]arene–toluene complex (**1**–**3**), for which a crystal structure is known,[45] arrangements **(1–3)A** (CH$_3$-group pointing inside the cavity) and **(1–3)B** (CH$_3$-group pointing outside the cavity) are of similar relative energy (ΔE = 0.2 kcal mol^{-1}). For **(1–3)A** CISs of −3.65 ppm (GIAO-DFT(B3LYP)/3-21G//MMFF) and −4.47 ppm (GIAO-DFT(B3LYP)/6-31G(d)//MMFF), respectively, are calculated, in reasonable agreement with the experimentally observed CIS of −6.2 ppm. In contrast, structures **(1–3)B** and **(1–3)C** do not give such good agreements (for graphical representations of CISs *cf.* ESI†). An overlay of both experimentally determined[45] and theoretically derived structures is shown in Fig. 4. The geometry of the calixarene host is well reproduced by the force field calculations, not taking the disorder of the ^{t}Bu groups into account. The toluene guest is tilted in the calculated structure (72°) towards the reference plane formed by the methylene bridges of the calixarene (plane A in Scheme 1). In the experimental structure, the longitudinal axis of the guest molecule is nearly perpendicular to this plane.



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Scheme 1 Reference planes used for the description of *p-tert*-butylcalix[4]arene–solvent complexes.

The complexation of toluene inside the cavity of *p-tert*-butylcalix[4]arene is not a static but a dynamic process as was demonstrated in a careful study by Ripmeester *et al.*[8] At room temperature the guest molecule is spinning rapidly around the longitudinal axis (10^8 Hz), leading to averaged signals even in the solid-state NMR spectra. Furthermore, at 150 K the methyl group of about 5–10% of the toluene molecules is pointing outside the cavity similar to structure **(1–3)B**. For this arrangement a downfield shift of 0.6 ppm (δ_{solid} = 21.9, δ_{liquid} = 21.3 ppm) has been observed.[8] According to this experimental observation nearly no CIS was calculated for **(1–3)B** (Table 3).

For THF (**4**) as a guest molecule, three minima structures **(1–4)A**, **(1–4)B** and **(1–4)C** with E_{rel} = 0.0–0.9 kcal mol^{-1} could be identified by the force field optimizations. The four different experimentally observed CIS values (Table 1, entry 3) indicate an unsymmetrical inclusion mode with the oxygen atom of the guest pointing outside of the cavity. Structures **(1–4)A** and **(1–4)C** agree best with the observed CIS pattern for THF according to our calculations. No direct comparison with an experimental single crystal structure determination deposited with the Cambridge Crystallographic Structure Database (CCSD)[46] is possible for **1**–**4**. In Fig. 5 an overlay of the calculated geometry of **1**–**4** with a comparable THF complex of a *p*-*tert*-butylcalix[4]arene-derivative is shown.[47] Again, the calculated and experimentally observed geometries of the host are in good agreement. The longitudinal THF axis through the oxygen atom is tilted against plane A (59.6°). A similar tilt (58.5°) can be found in the crystal structure. Comparison of geometries (**1**–**4**)**B** and (**1**–**4**)**A** or (**1**–**4**)**C**, respectively, also show that slight changes in the spatial arrangements of host and guest result in large differences in the calculated NMR chemical shifts.

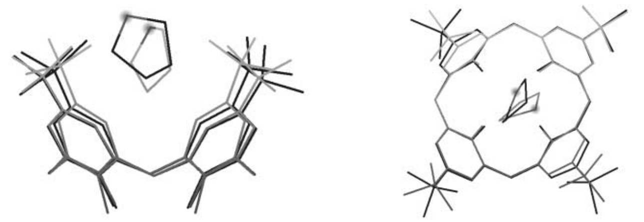

Fig. 5 Overlay of the structures of the *p*-*tert*-butylcalix[4]arene–THF complex obtained by single crystal structure determination (gray) of the dimethoxy*p*-*tert*-butylcalix[4]arene–THF–Fe^{II} solvate[47] by MMFF geometry optimization (black; (**1**–**4**)**C**); hydrogen atoms are omitted for clarity; left: side view, right: top view.

FT-IR spectroscopy showed that the guest molecule is highly mobile and disordered when acetone (**5**) is used for preparation of the host–guest complex. Accordingly, the solid-state NMR spectra of complex **1**–**5** gave only two CIS values, one for each type of carbon atom. In this case it is difficult to decide which of the three structures (**1**–**5**)**A**, (**1**–**5**)**B** and (**1**–**5**)**C** corresponds to the real structure in the solid-state NMR experiment. Again, no X-ray structure was available in the CCSD and therefore Fig. 6 shows an overlay with the X-ray structure of a comparable complex.[48]

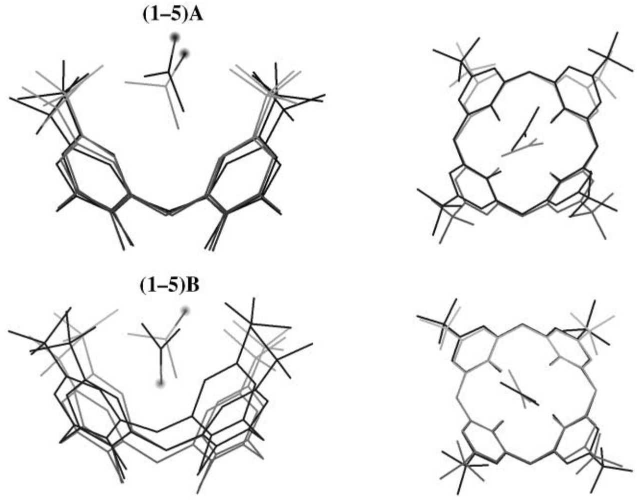

Fig. 6 Overlay of the structures of the *p*-*tert*-butylcalix[4]arene–acetone complex obtained by single crystal structure determination (gray) of the *cis*-5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,14-*bis*(4-nitrophenyl)calix[4]arene–acetone solvate[48] by MMFF geometry optimization (black; (**1**–**5**)**A**, (**1**–**5**)**B**); hydrogen atoms are omitted for clarity; left: side view, right: top view.

In general, the calix[4]arene skeleton itself and the relative arrangement of the guest in the host cavity is described very well by optimizations using the Merck94 force field. However, the extent of inclusion is underestimated in all cases studied. A statistical survey of solvent complexes of *p*-*tert*-butylcalix[4]arene derivatives deposited with the CCSD[46] showed that the nearest carbon atom of the guest is usually located close to the reference plane A (mean distance = 2.882 ± 0.016 Å; for detailed data *cf.* ESI †). In all calculated structures this distance is somewhat larger (3.2–3.4 Å) underestimating the extent of inclusion. However, the presented methodology is a very sensitive tool for the analysis and characterization of possible host–guest geometries.

Conclusion

In summary, GIAO-DFT calculations of complexation-induced chemical shifts of supramolecular host–guest complexes based on MMFF optimized structures is a fast and sensitive computational approach for the identification of possible spatial arrangements of such assemblies. This methodology does not require any special computational adaptation; only standard commercial program packages were used. Furthermore, this approach is not limited to certain classes of compounds, and any nucleus for which experimental CIS values are available can be used as a probe either in the solid state or in solution. However, the applicability is limited by the quality of the experimental data available because only stationary geometries can be studied. For complexes which have included guests that are in rotational motion, statistical treatment of the systems using molecular dynamics simulations followed by NMR calculations for selected structures might be an appropriate method to simulate the experimental averaging of the CIS.

Experimental

p-*tert*-Butylcalix[4]arene complexes **1**–**2**, **1**–**3**, **1**–**4** and **1**–**5** were prepared and characterized as reported previously.[17,26]

Geometry optimizations using the Merck94 force field were performed with the PC Spartan Pro program package.[49] Standard convergence criteria as implemented in the modeling program without using any geometry constraints were applied. *Ab initio* geometry optimizations using HF/6-31G(d) and single point property calculations using DFT methods were performed with the Gaussian98 program package[50] based on the geometries obtained by the Merck94 force field (MMFF) optimizations.

Acknowledgements

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