

Supplementary Information

The mutual influence of non-covalent interactions in π -electron deficient cavity: the case of anion recognition by tetraoxacalix[2]arene[2]triazine

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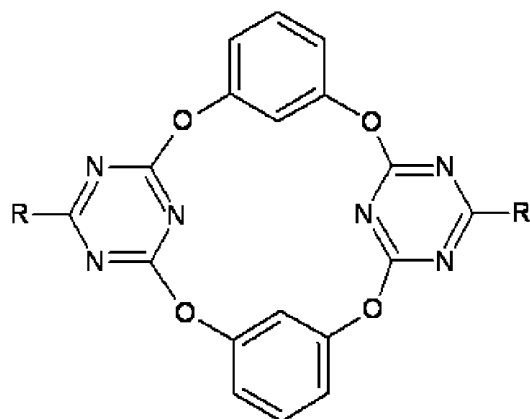
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Binding energies (kcal/mol) without and with BSSE correction (E and E_{BSSE} respectively)

	F-		Cl-		Br-	
	1_{binary}	1_{ternary}	1_{binary}	1_{ternary}	1_{binary}	1_{ternary}
E	-42.5	-65.3	-30.0	-45.8	-28.2	-42.6
E_{BSSE}	-39.4	-58.4	-27.0	-39.7	-24.2	-35.5

Schematic structure of dichloro-substituted tetraoxacalix[2]arene[2]triazine 1 and tetraoxacalix[2]arene[2]triazine 2



1, R = Cl
2, R = H

Additional computational details

Electronic structure calculations have been performed with Turbomole Package¹ (version 5.10) using second-order Möller-Plesset perturbation theory (MP2) within the approximation resolution of identity MP2 (RI-MP2)². Geometries have been optimized using the augmented correlation consistent double- ζ basis set (aug-cc-pVDZ)³ for the halide and oxygen atoms, whereas standard valence double- ζ basis set (cc-pVDZ)⁴ have been utilized for C, H and N atoms. No symmetry constraints have been imposed for the π -anion interactions between anions (fluoride, chloride, bromide) and tetraoxacalix[2]arene[2]triazine.

The crystal structure of the ternary complex incorporating the host, a halide ion and a water molecule were taken from The Cambridge Crystallographic Data Centre.^{5,6} The structure of the host with fluoride ion and water was built from the corresponding structure containing chloride.

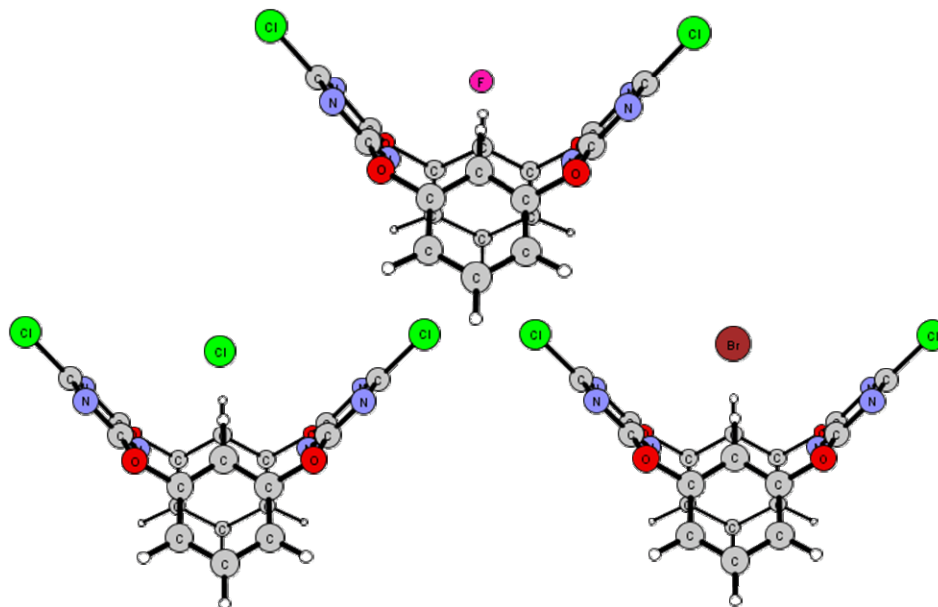
The binary structures containing host molecule and halides were constructed putting the halide atom at the centre of host molecule.

The minimum nature of both binary and ternary complexes and also of all model systems has been confirmed by frequencies calculations at the same level of theory.

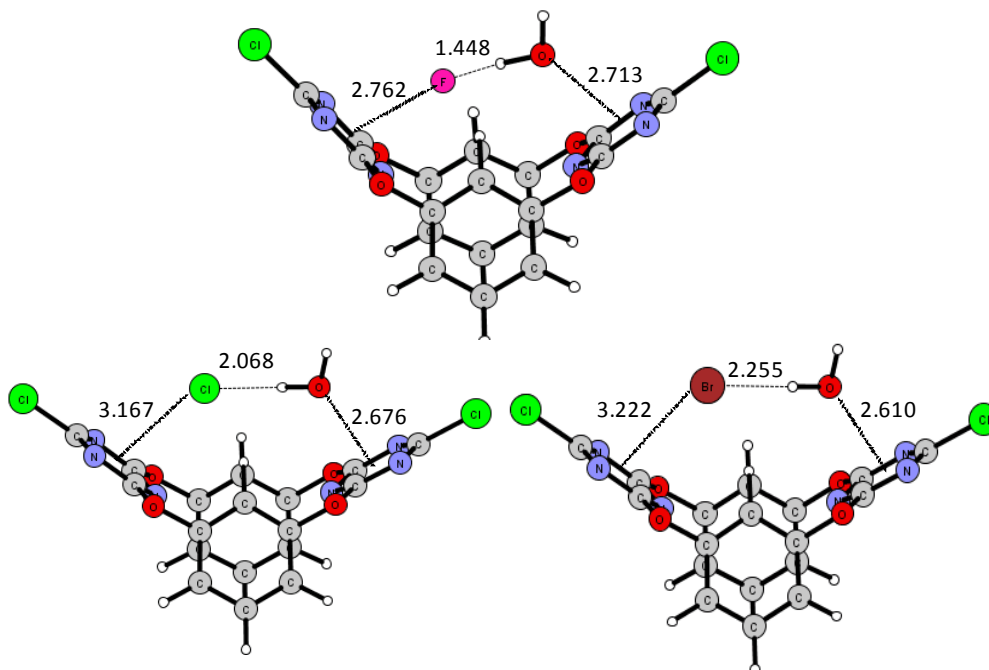
The binding energies, calculated at the RI-MP2 level of theory, were corrected for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.⁷

Optimized structures and selected geometric parameters of **1**_{binary} and **1**_{ternary} complexes

1_{binary} complexes



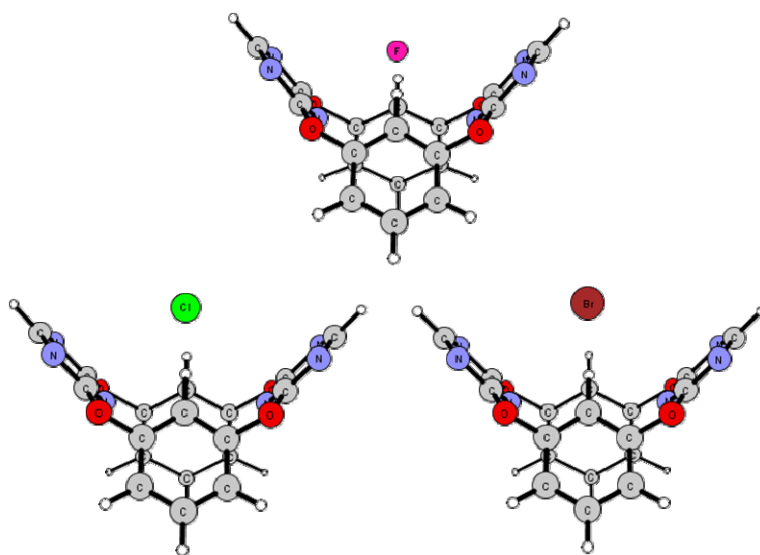
1_{ternary} complexes



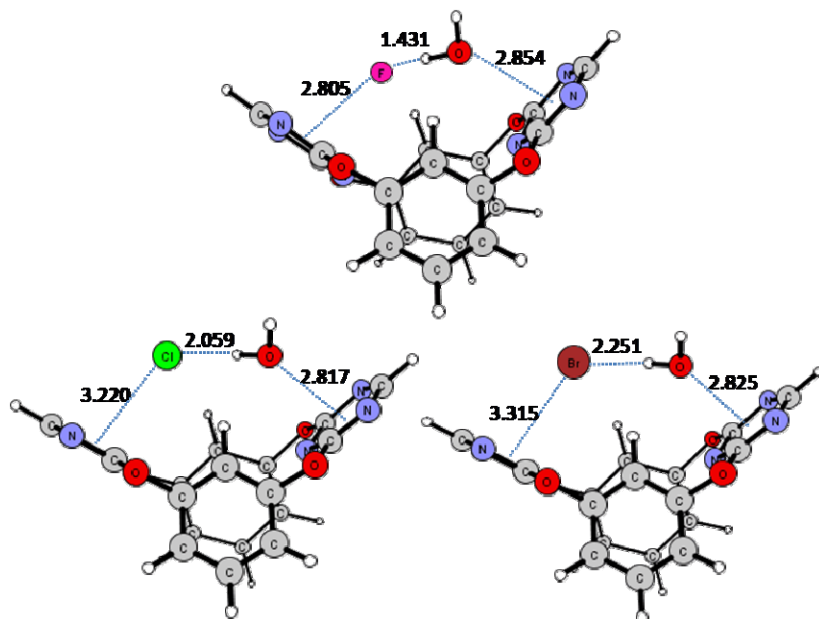
Optimized structures, binding energies and selected geometric parameters of 2_{binary} and 2_{ternary} complexes

	F^-		Cl^-		Br^-	
	2_{binary}	2_{ternary}	2_{binary}	2_{ternary}	2_{binary}	2_{ternary}
E (kcal/mol)	-36.6	-58.8	-25.1	-39.8	-23.5	-36.8
E_{BSSE} (kcal/mol)	-33.5	-52.3	-22.1	-33.9	-19.7	-30.0

2_{binary} complexes



2_{ternary} complexes

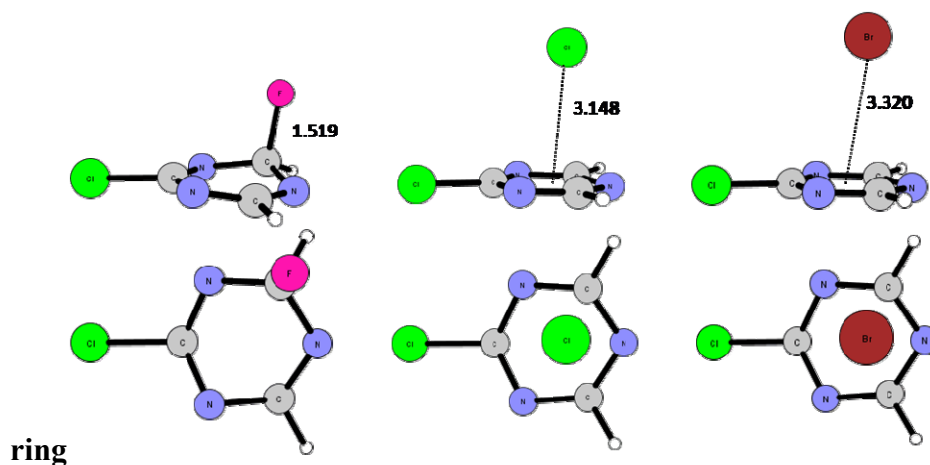


Optimized structures of all considered non-covalent interactions

- H bond between halides (F^- , Cl^- , Br^-) and water molecule

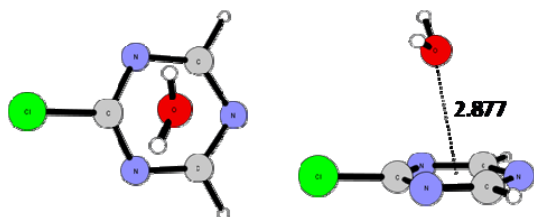


- Anion- π interaction of halides ($*F^-$, Cl^- , Br^-) with triazine ring

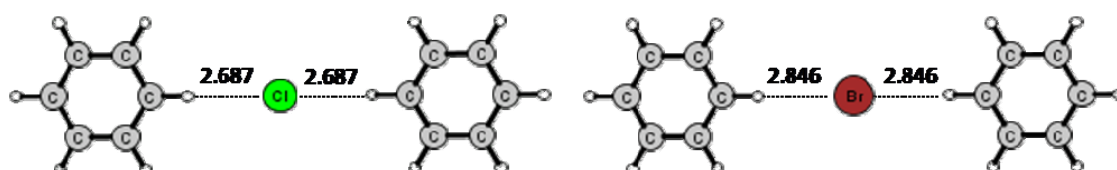


* only a strong σ -complex was observed for Fluoride-triazine interaction

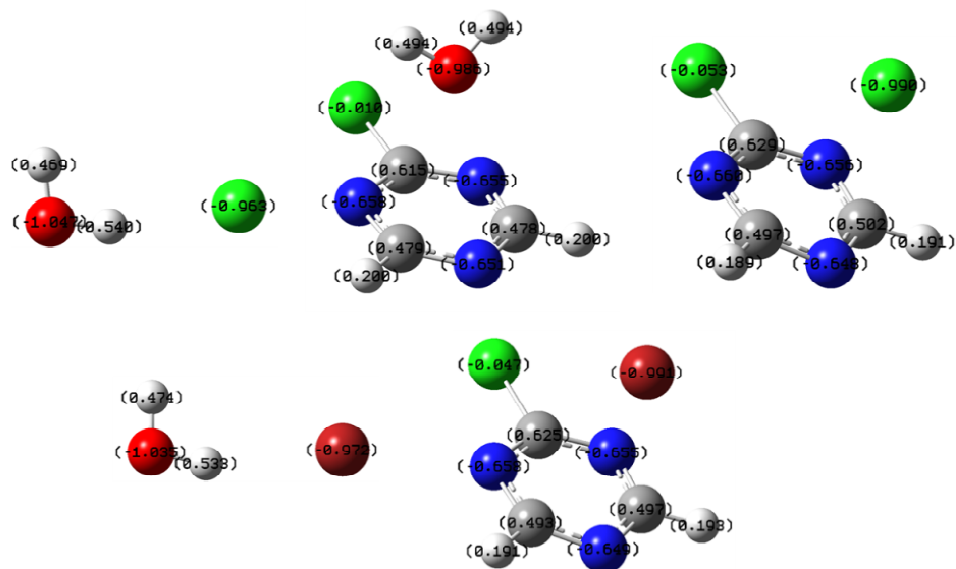
- Lone-pair- π interaction between water and triazine ring



- Arene C-H hydrogen bonds with the halide (Cl^- , Br^-) guests

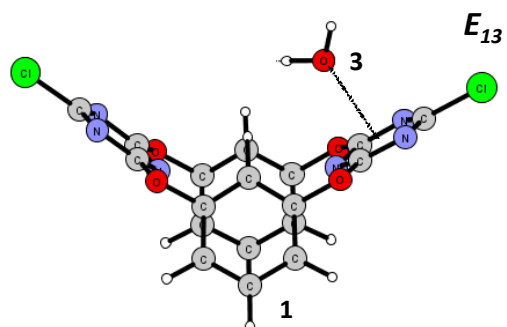
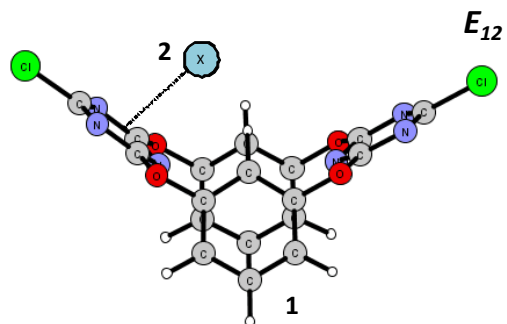


NBO charges analysis for selected non-covalent interactions involved in both 1_{ternary} complexes, with Cl⁻ and Br⁻



Models used for (E_{12} , E_{13} , E_{23}) calculations and energy values

	Cl^-			Br^-		
	E_{12}	E_{13}	E_{23}	E_{12}	E_{13}	E_{23}
E (kcal/mol)	-27.3	-3.3	-13.7	-25.4	-3.8	-11.9
E_{BSSE} (kcal/mol)	-24.6	-0.5	-13.1	-21.9	-1.0	-11.0



References

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