Supporting Information

A Theoretical Study of the Insertion of Atoms and Ions into Titanosilsequioxane (Ti-POSS) in Comparison with POSS

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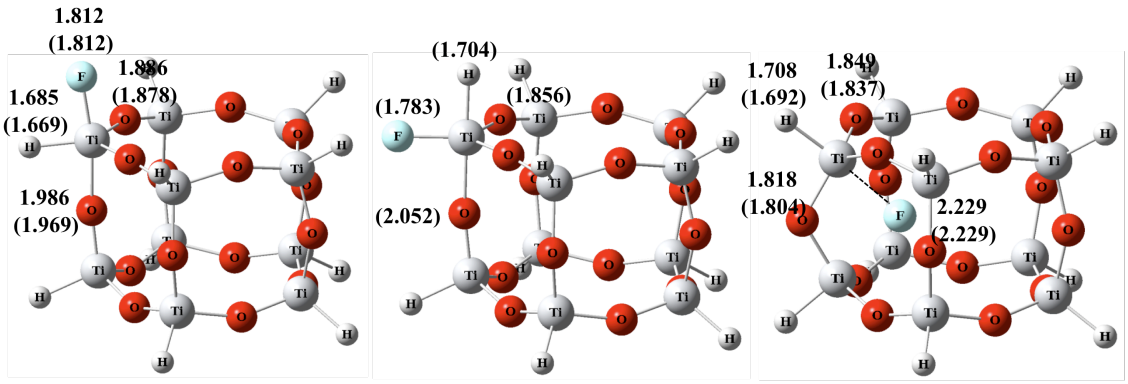
Contents

1. Cage Effect in $F^-@T_n$ (n=8 and 10)

In order to understand the endohedral complex of F^- and Ti-T_8 ("endo" (e)) more deeply, we have investigated "cage effect" by comparison of the exohedral and endohedral complexes of Ti-T_n (n=8 and 10) with those with the model compound $FH(TiOH)_3^-$ as shown in Figure S3. The geometrical parameters and the relative energies of the three types of complexes are depicted in Table S2. The "equatorial" is least stable in all cases and it disappeared at the B3LYP level for $FH(TiOH)_3^-$ and F^-(Ti-T_{10}) but the relative stability between "axial" and "endo" is not regular. The stability of "endo" structure is larger in the cage compounds (especially in Ti-T_8) than in $FH(TiOH)_3^-$. This may be just a "cage effect". Here, it may be worth to examine the effect in more detail. For "endo" structure, the averaged distance between F^- and skeletal Ti atoms (see Table S2) in T_8 is shorter than that in T_{10} as expected. In spite of the shorter $r(F^-Ti)_{ave}$, however, the absolute value of the interaction energy (ΔE_{int}) of "endo" in F^-@Ti-T_8 is rather smaller than that in F^-@Ti-T_{10}, which is also true for the other isomers as shown in Tables 6 and S1. This seems to cause the larger absolute value of the binding energy (ΔE_{comp}) of the isomers of Ti-T_{10} compared to those of Ti-T_8 except for the "endo". On the other hand, ΔE_{def} is slightly larger in Ti-T_{10} compared with that in Ti-T_8. These results seem to indicate the significant softness of the Ti-T_n with larger cage, which allows the strong interaction with the guest species accompanying the local deformation of the cage. The smaller ΔE_{def} in "endo" of Ti-T_8 than that in Ti-T_{10} seems to make the structure most stable among the isomers in the former.



axial C_S **equatorial C_S** **endo C_S**

Figure S1: The B3LYP/6-311+G(d) and HF/6-311+G(d) (in parentheses) optimized geometries of two types of the exohedral ("axial" and "equatorial") and endohedral ("endo") complexes of F^- and Ti-T_{10} in angstroms.

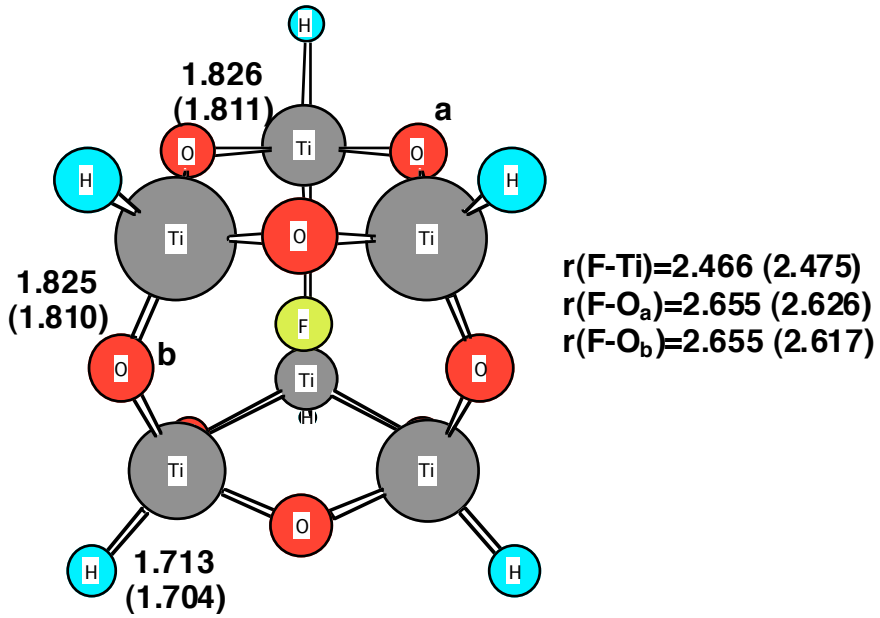


Figure S2: The B3LYP/6-311+G(d) and HF/6-311+G(d) (in parentheses) optimized geometries of the endohedral complex (D_{3h}) of F^- and Ti-T_6 in angstroms.

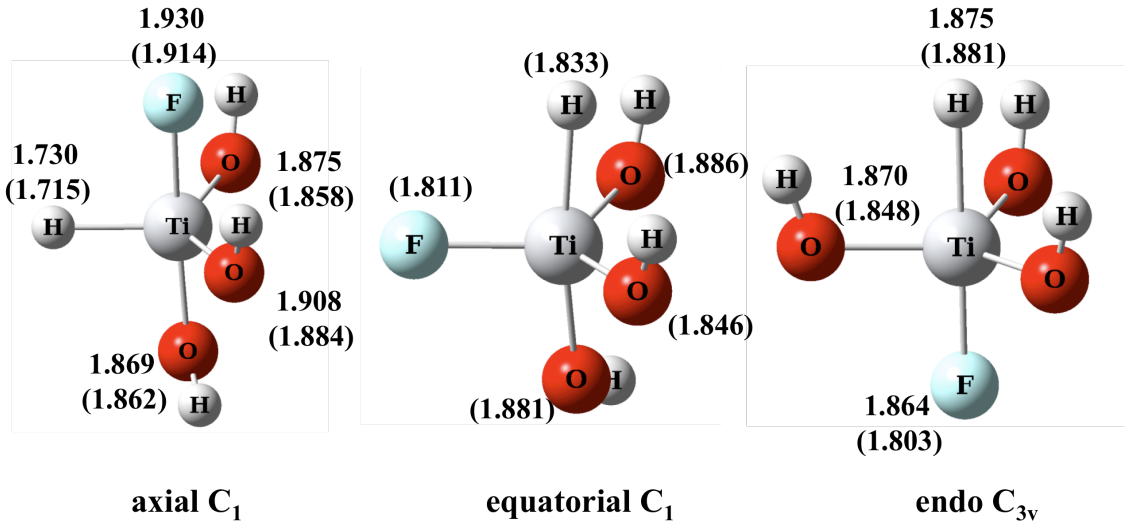


Figure S3: The B3LYP/6-311+G(d) and HF/6-311+G(d) (in parentheses) optimized geometries of three isomers of the model compound, $FHTi(OH)_3^-$ in angstroms.

TABLE S1: Energy decomposition of the binding energy (ΔE_{comp}) (kcal/mol) of the complexes of F^- and Ti-T_8/Ti-T_{10} and the energies relative to "axial" (ΔE) in each system based on the B3LYP/6-311+G(d)+ZPC, MP2/6-311+G(d)//B3LYP/6-311+G(d) [a] and B3LYP/6-311+G(d)//HF/6-311+G(d)[b] energies.

	isomer	Sym	ΔE_{def}	ΔE_{int}	ΔE_{comp}	ΔE_{comp}+ZPC	ΔE
F^-+Ti-T_8	(a) axial	C_1	35.9	-135.1	-99.1	-98.4	0.0[*0.0*]
		(Cs)	(34.7)	(-133.4)	(-98.7)		(0.0)
	(b) equatorial	Cs	55.6	-150.6	-95.0	-94.8	3.6
		(Cs)	(50.6)	(-145.0)	(-94.4)		(4.3)
	(c) neighbor bridge	C_1	56.3	-151.4	-95.1	-93.7	4.7
		(C_1)	(52.2)	(-146.3)	(-94.1)		(4.6)
	(d) diagonal bridge	C_{2v}	63.9	-149.5	-85.6	-84.7	13.7
		(C_{2v})	(60.4)	(-145.7)	(-85.3)		(13.4)
	(e) endo	C_1	23.2	-125.3	-102.1	-101.6	-3.2[*-7.6*]
		(Cs)	(14.7)	(-115.8)	(-101.2)		(-2.5)
F^-+Ti-T_{10}	(a) axial	Cs	36.2	-137.9	-101.7	-100.8	0.0
		(Cs)	(35.1)	(-136.2)	(-101.1)		(0.0)
	(b) equatorial	-	-	-	-	-	-
		(Cs)	(54.1)	(-150.4)	(-96.3)		(4.8)
	(c) endo	Cs	27.1	-128.2	-101.1	-100.5	0.3
		(Cs)	(20.9)	(-121.2)	(-100.3)		(0.8)

[a]The values in italics are in square brackets.

[b]The values are in parentheses.

TABLE S2: The B3LYP/6-311+G(d) and HF/6-311+G(d) [a] geometrical parameters (Å) and the B3LYP/6-311+G(d)+ZPC and MP2/6-311+G(d) [b] relative energies (kcal/mol) of three isomers of F^- + Ti-T_n(n=8 and 10) and $FHTi(OH)_3^-$.

		sym	r(F-Ti)	r(H-Ti)	r(O-Ti)$_1$	r(O-Ti)$_2$	r(O-Ti)$_3$	r(F-Ti)$_{ave}$ [c]	ΔE
$FHTi(OH)_3^-$	axial	C_1	1.930	1.730	1.875	1.908	1.869		0.0
		(C_1)	(1.914)	(1.715)	(1.858)	(1.884)	(1.862)		(0.0)
	equatorial	-	-	-	-	-	-		-
		(C_1)	(1.811)	(1.833)	(1.886)	(1.846)	(1.881)		(3.8)
	endo	C_{3v}	1.864	1.875	1.870	1.870	1.870		1.2
		(C_{3v})	(1.803)	(1.881)	(1.848)	(1.848)	(1.848)		(2.5)
F^-+(Ti-T_8)	axial	C_1	1.814	1.690	1.884	1.885	1.986		0.0[*0.0*]
		(Cs)	(1.813)	(1.676)	(1.876)	(1.876)	(1.968)		(0.0)
	equatorial	Cs	1.788	1.717	1.862	1.862	2.088		3.6
		(Cs)	(1.789)	(1.706)	(1.854)	(1.854)	(2.052)		(4.3)
	endo	C_1	2.321	1.708	1.837	1.838	1.821	3.068	-3.2[*-7.6*]
		(Cs)	(2.219)	(1.695)	(1.827)	(1.827)	(1.827)	(3.076)	(-2.5)
F^-+(Ti-T_{10})	axial	Cs	1.812	1.685	1.886	1.886	1.986		0.0
		(Cs)	(1.812)	(1.669)	(1.878)	(1.878)	(1.969)		(0.0)
	equatorial	-	-	-	-	-	-		-
		(Cs)	(1.783)	(1.704)	(1.856)	(1.856)	(2.052)		(4.8)
	endo	Cs	2.229	1.708	1.849	1.849	1.818	3.696	0.3
		(Cs)	(2.229)	(1.692)	(1.837)	(1.837)	(1.804)	(3.695)	(0.8)

[a]The HF/6-311+G(d) values are in parentheses.

[b]The values in italics are in square brackets.

[c]The averaged distance between F^- and all skeletal Ti atoms of the cages.