Electronic Supplementary Material (ESI) for RSC Advances.

Table S1. The composition (%) of X groups, the Si_{18} skeleton and the inserted atom (Si_C/Ge) to the HOMO and LUMO of $Si_{18}X_{12}$, $Si_{19}X_{12}$ and $Si_{18}GeX_{12}$; the Mulliken method has been used to derive the compositions.

	X group	HOMO			LUMO		
		X	Si_{18}	Si_C/Ge	X	Si_{18}	Si_C/Ge
Si_{18}	H	8.7	91.3	-	0.0	100.0	-
	F	8.0	92.0	-	2.3	97.7	-
	Cl	15.7	84.3	-	5.2	94.8	-
	Br	20.6	79.4	-	7.2	92.8	-
	OH	9.7	90.3	-	5.7	94.3	-
	NH_2	16.1	83.9	-	8.6	91.4	-
	COOH	18.3	81.7	-	4.7	95.3	-
Si_{19}	H	4.9	71.6	23.5	0.0	97.6	2.4
	F	5.8	92.9	1.3	1.2	96.0	2.7
	Cl	9.2	89.2	1.6	5.9	93.4	0.8
	Br	11.7	86.5	1.8	7.8	91.3	0.8
	OH	10.4	89.1	0.6	1.0	96.6	2.5
	NH_2	11.8	87.5	0.7	7.2	92.5	0.2
	COOH	6.3	84.6	9.1	7.7	90.5	1.8
$Si_{18}Ge$	H	7.5	58.9	33.6	0.0	98.2	1.8
	F	5.4	92.6	2.0	1.4	77.7	20.9
	Cl	9.0	89.4	1.6	6.0	93.5	0.5
	Br	11.8	86.8	1.4	7.9	91.6	0.4
	OH	9.8	89.4	0.8	3.4	77.5	19.1
	NH_2	12.0	86.6	1.4	8.1	91.3	0.6
	COOH	5.1	92.1	2.8	7.6	91.0	1.4

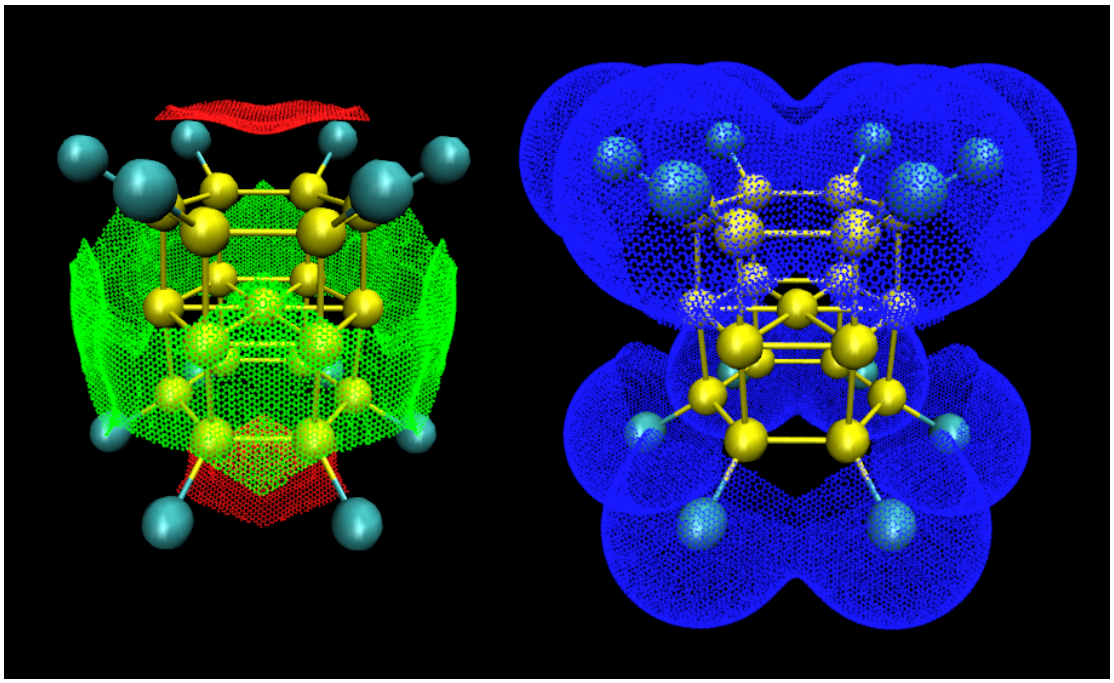

Figure S1. Illustration of partition of the vdW surface for the investigated silicon clusters. $Si_{19}Cl_{12}$ is taken as example. Red, green, and blue correspond to local vdW surface of the two-ends region, equatorial region and X group region, respectively.

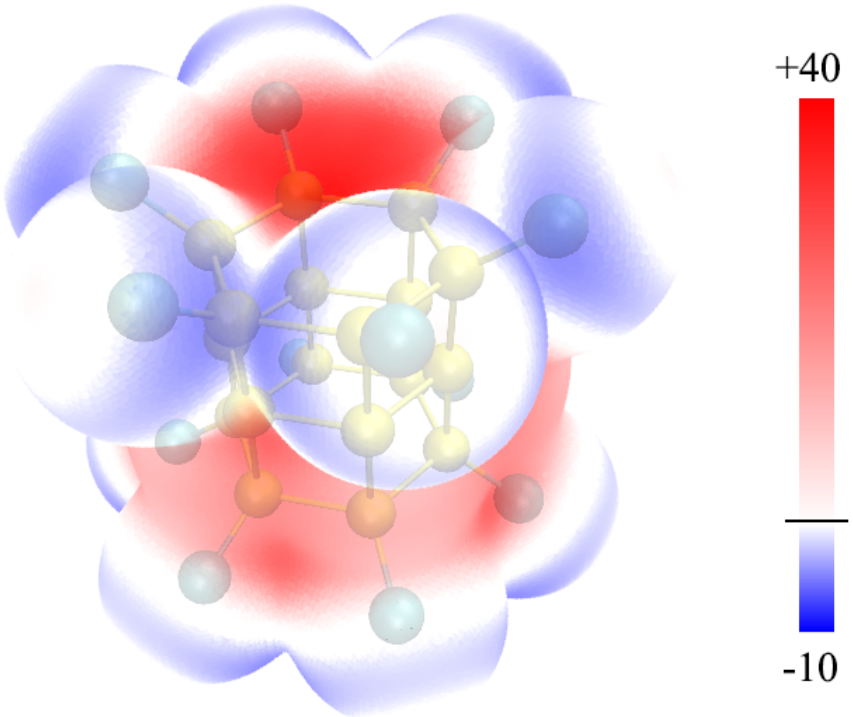

Figure S2. Electrostatic potential (ESP) mapped with the vdW surface of $Si_{18}Cl_{12}$. The value is in kcal/mol. The vdW surface is defined as the isosurface with $\rho = 0.001$ a.u.

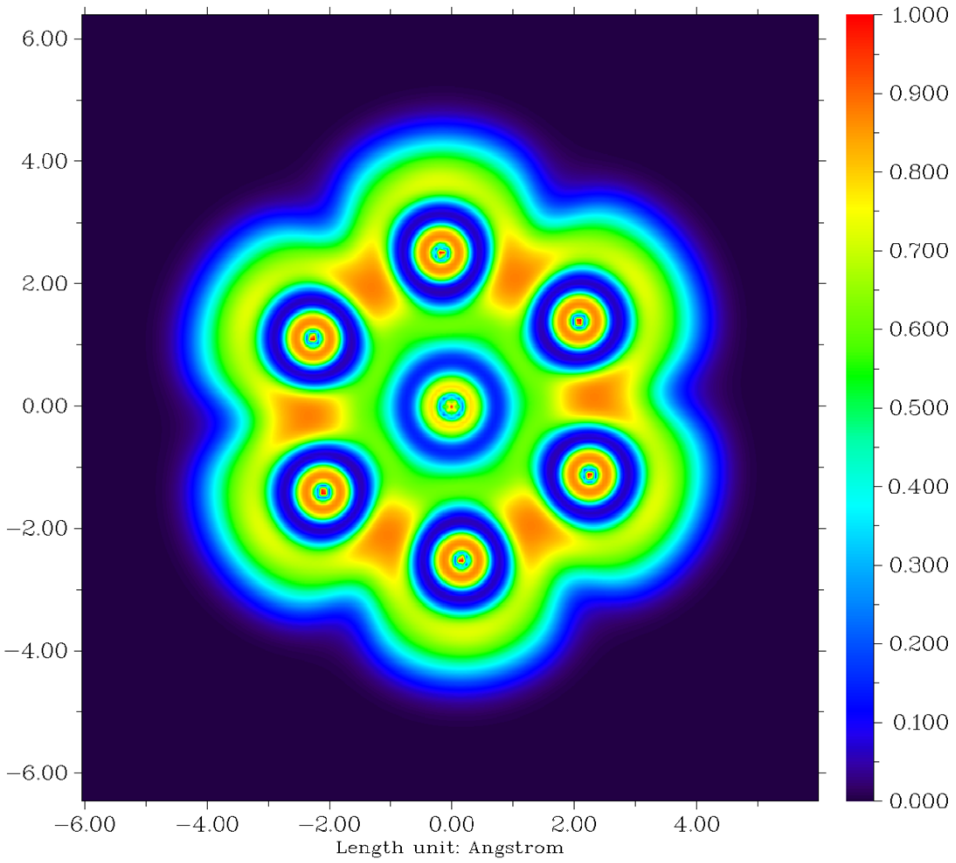

Figure S3. ELF map of the middle-layer of $Si_{18}GeCl_{12}$.

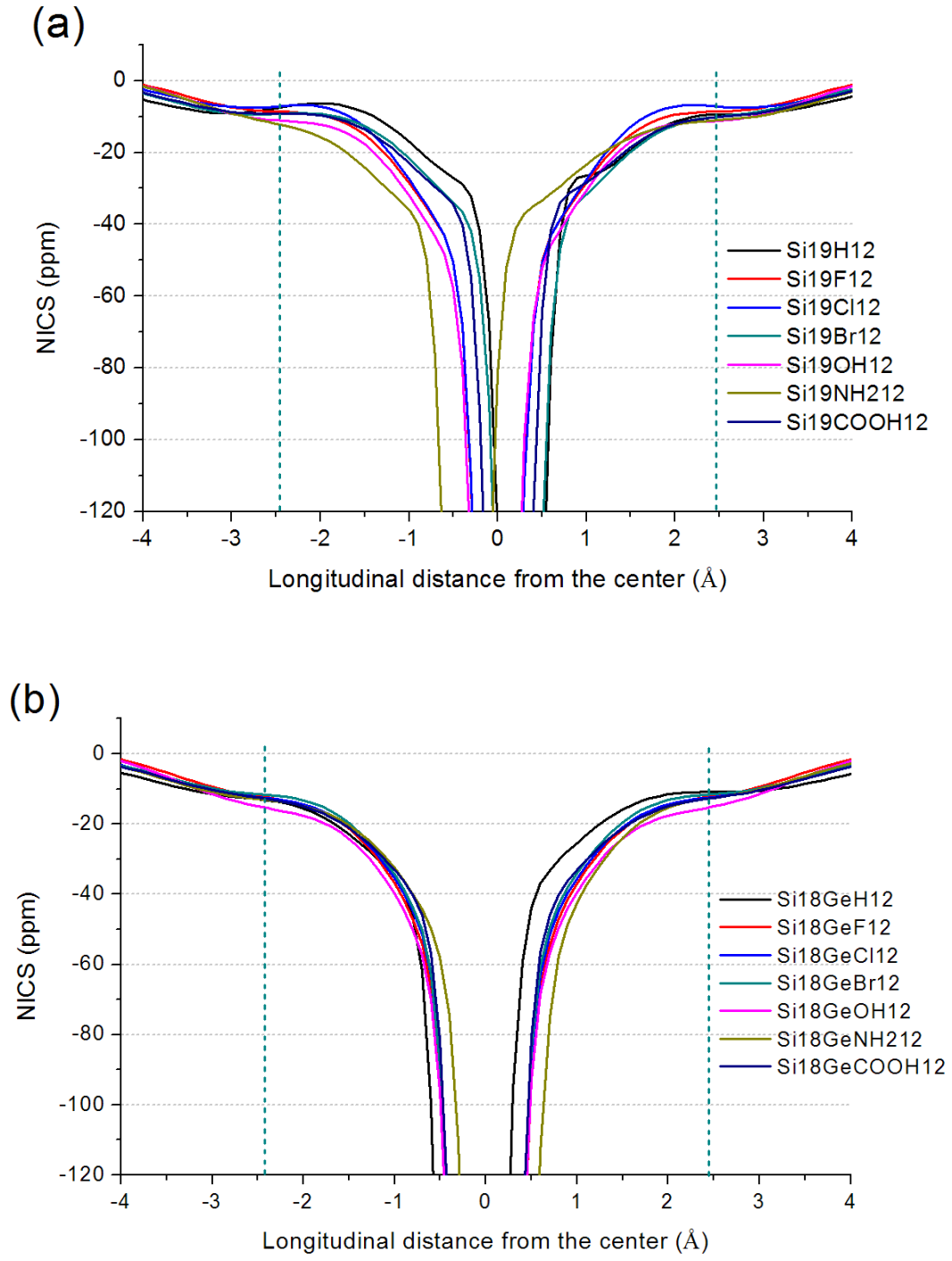

Figure S4. NICS curves along the symmetry axis of $Si_{19}X_{12}$ (a) and $Si_{18}GeX_{12}$ (b) nanoclusters. The vertical dashed lines correspond to the approximate position of the peripherical silicon atoms.