Supporting Information Available

Evolutionary chlorination of graphene: from charge-transfer complex to covalent bonding and non-bonding

Table S1. Calculated properties for Cl monomer and dimer adsorption on graphene in a 4 × 4 supercell: binding energies per adsorbed atom (E_b), total magnetic moments (M), charge transfer of Cl atoms from Bader charge analysis (Δq_{Cl}), distance between Cl atom and the C atom below ($d_{C–Cl}$), and distance between two Cl atoms within one unit cell ($d_{Cl–Cl}$).

System		E_b (eV)	M (μB)	Δq_{Cl} (e)	$d_{C\text{-}Cl}$ (Å)	$d_{Cl\text{-}Cl}$ (Å)
Monomer	A_0	-1.13	0.52	+0.44	2.53	
Dimer	A_0-B_1	Not stable*				
	A_0-A_2	-1.85 (Cl_2)	0	+0.04,-0.06	3.21	1.98
	A_0-B_3	-1.22	0	+0.21,+0.19	1.94	3.21
	A_0-B_4	-1.01	0	+0.39, +0.13	1.96, 2.50	3.72
	A_0-A_5	-0.96	0.65	+0.32, +0.32	2.41	4.33
	A_0-A_6	-0.95	1.17	+0.32, +0.32	2.43	5.05
	A_0-B_7	-1.13	0	+0.23, +0.26	2.01, 2.05	5.70

* A_0-B_1 configuration is exceptional because it is too close to accommodate two Cl atoms: the sum radius of two Cl atoms is 1.98 Å, much larger than the C-C bond distance of 1.42 Å.

Table S2. Calculated properties for homogeneous adsorption of Cl atoms on one side of graphene with various atomic coverages in a 4 × 4 supercell: binding energies per atom (E_b), total magnetic moments (M), charge transfer of Cl atoms from Bader charge analysis (Δq_{Cl}), lattice constant (a), and characteristic atomic distances ($d_{C–Cl}$, $d_{C–C,}$ and $d_{Cl–Cl}$). $d_{C–C}$ is the bond distance of the C atom below Cl and the nearest neighbor. The types of bonding are specified for the adsorption: non-bonding (NB), covalent bonding (CB), and charge-transfer complex (CTC).

System	bonding	E_b (eV)	M (μ_B)	Δq_{Cl} (e)	a (Å)	$d_{C\text{-}Cl}$ (Å)	$d_{C\text{-}C}$ (Å)	$d_{Cl\text{-}Cl}$ (Å)
CCl	Not stable							
C_2Cl	NB	-1.34	0	+0.03	2.50	3.37	1.44	2.50
C_4Cl	NB	-1.48	0	+0.07, + 0.11	2.43	3.24	1.40	2.81
	CB	-1.14	0	+0.15	2.48	1.88	1.49	2.86
C_8Cl	CTC	-0.87	0.65	+0.27	2.45	2.29	1.43	4.90
$C_{16}Cl$	CB	-1.13	0	+0.22, +0.26	2.45	2.04	1.46	5.66

Table S3. Calculated properties of homogeneous Cl adsorption on both sides of graphene with a 4 × 4 supercell. See Table S2 caption for definition of various quantities.

		E_b (eV)	M (μ_B)	Δq_{Cl} (e)	a (Å)	$d_{C\text{-}Cl}$ (Å)	$d_{C\text{-}C}$ (Å)	$d_{Cl\text{-}Cl}$ (Å)
CCl	NB	-1.39	0	+0.01	2.52	3.36	1.46	2.53
	CB	-0.84	0	+0.01	2.85	1.74	1.72	2.85
C_2Cl	NB	-1.46	0	+0.06, +0.07	2.42	3.53	1.40	2.80
	CB	-1.34	0	0.00, +0.06	2.52	1.84	1.50	2.84,3.05
C_4Cl	CB	-1.61	0	+0.11	2.45	1.85	1.47, 1.51	4.90
C_8Cl	CB	-1.48	0	+0.17	2.45	1.89	1.47	5.50
$C_{16}Cl$	CB	-1.56	0	+0.18	2.45	1.89	1.47,1.50	9.80