Supporting Information for

Bromine polycondensation in pristine and fluorinated graphitic carbons

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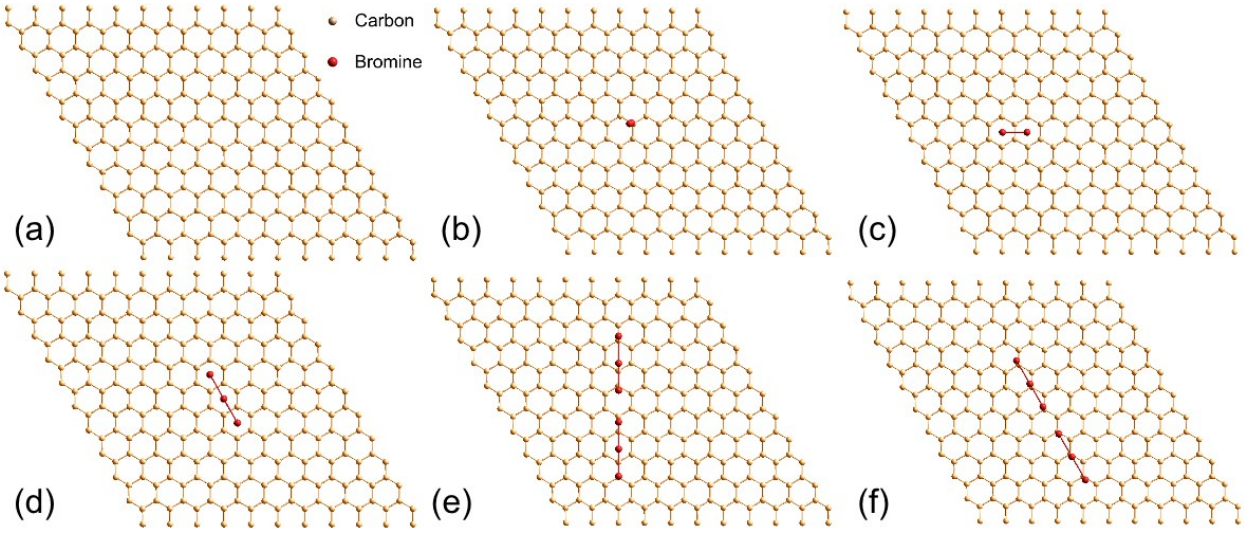


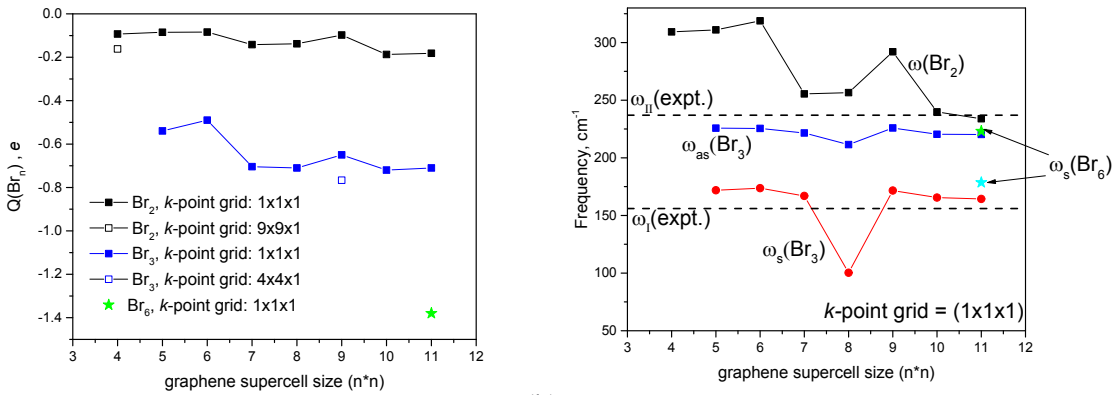
Fig. S1 Optimized geometries of graphene supercell (a), Br_2 oriented perpendicular (b) and paralllll (c) to graphene sheet, Br_3 (d), and Br_6 (i,j) over graphene sheet.

Table S1 Comparison of stretching frequencies of Br_3 over graphene obtained using LDA within spin-averaged and spin-polarized approaches.

kt	$S_{av.}/S_{pol.}$	$E^{tot}_{spin\ av.}$-$E^{tot}_{spin\ pol.}$	$\nu_{spin.\ av.}$ / $\nu_{spin\ pol.}$
0.04	0/0.002	0 eV	ν_3^s=164/164 cm^{-1}; ν_3^a =220/220 cm^{-1}
0.01	0/1	0.1 eV	ν_3^s=164.5/166.1 cm-1; ν_3^a=222/220.3 cm^{-1}

Table S2 Dependence of calculated parameters for the Br_2 in parallel orientation to graphene sheet on the size of unit cell and k-point grid.

graphene cell size	*k*-point grid	$Q_{Br_2}(e)$	ν_2^s (cm^{-1})
4×4	1×1×1	-0.09296	309.2126
4×4	9×9×1	-0.161316	258.1
5×5	1×1×1	-0.08489	310.97708
6×6	1×1×1	-0.084	318.84834
7×7	1×1×1	-0.14167	255.47528
8×8	1×1×1	-0.13815	256.54681
9×9	1×1×1	-0.09754	291.92995
10×10	1×1×1	-0.18717	239.85602
11×11	1×1×1	-0.18168	233.89082



(a) (b)

Fig. S2 Variation in calculated charge (a) and stretching frequencies (b) of Br_2, Br_3 and Br_6 located over graphene sheet with the size of graphene supercell and k-point grid. Dashed lines in (b) correspond to peak I and II of experimental Raman spectra of brominated graphite and bromine-intercalated fluorinated graphites (see Fig. 1).

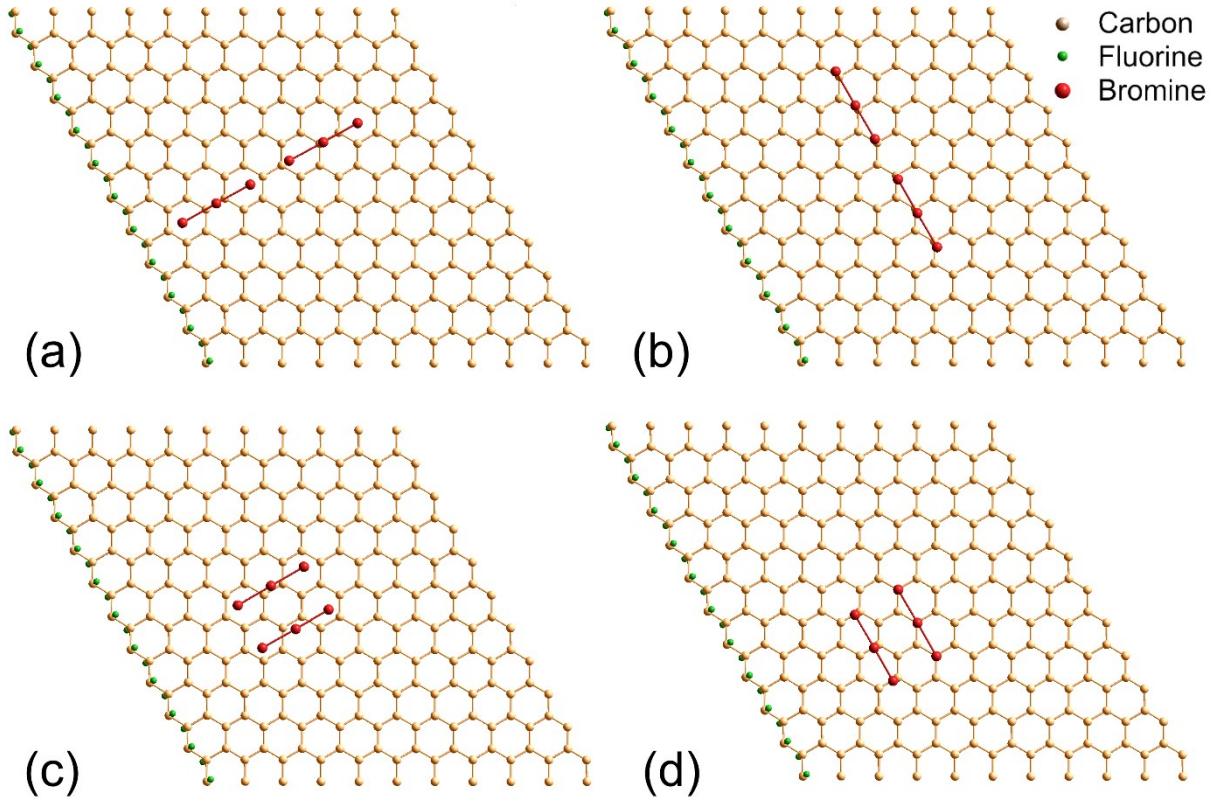


Fig. S3 Optimized geometries of metastable structures of Br_6 over partially fluorinated graphene sheet.

Table S3 Calculated binding energy E_b per one bromine atom (eV), charge transfer Q_{Br6} (e), and symmetrical stretching Br-Br frequencies ω_s (cm^{-1}) for the Br_6 over partially fluorinated graphene (see Fig. S3).

	E_b/Br (eV)	Q_{Br_6} (e)	$\nu_3^s - \nu_3^s$ / $\nu_3^a - \nu_3^a$ (cm^{-1})
(a)	-0.359	-1.25	162.9 / 227.3
(b)	-0.360	-1.28	159.6 / 225.2
(c)	-0.359	-0.65	179.0 / 230.1
(d)	-0.358	-0.59	181.9 / 231.1

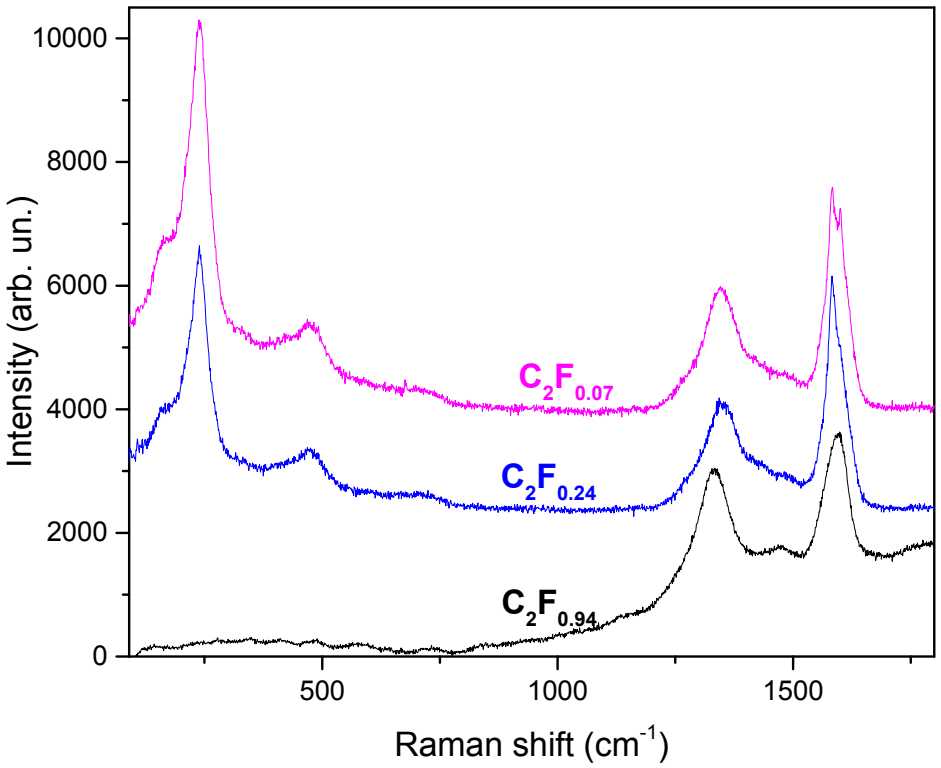


Fig. S4 Raman spectra taken at 514 nm for graphite intercalation compounds (C_2F_x-Br) synthesized without additional treatment with Br_2 vapors.