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 parallel (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.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$S_{av}/S_{pol}$</th>
<th>$\Delta E_{tot}^{spin av./spin pol.}$</th>
<th>$\nu_{spin av.}^{s}$</th>
<th>$\nu_{spin pol.}^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0/0.002</td>
<td>0 eV</td>
<td>164/164 cm$^{-1}$</td>
<td>220/220 cm$^{-1}$</td>
</tr>
<tr>
<td>0.01</td>
<td>0/1</td>
<td>0.1 eV</td>
<td>164.5/166.1 cm$^{-1}$</td>
<td>220.3/220 cm$^{-1}$</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>graphene cell size</th>
<th>k-point grid</th>
<th>$Q_{Br_2}$ (e)</th>
<th>$\nu_2^{s}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4×4</td>
<td>1×1×1</td>
<td>-0.09296</td>
<td>309.2126</td>
</tr>
<tr>
<td>4×4</td>
<td>9×9×1</td>
<td>-0.161316</td>
<td>258.1</td>
</tr>
<tr>
<td>5×5</td>
<td>1×1×1</td>
<td>-0.08489</td>
<td>310.97708</td>
</tr>
<tr>
<td>6×6</td>
<td>1×1×1</td>
<td>-0.084</td>
<td>318.84834</td>
</tr>
<tr>
<td>7×7</td>
<td>1×1×1</td>
<td>-0.14167</td>
<td>255.47528</td>
</tr>
<tr>
<td>8×8</td>
<td>1×1×1</td>
<td>-0.13815</td>
<td>256.54681</td>
</tr>
<tr>
<td>9×9</td>
<td>1×1×1</td>
<td>-0.09754</td>
<td>291.92995</td>
</tr>
<tr>
<td>10×10</td>
<td>1×1×1</td>
<td>-0.18717</td>
<td>239.85602</td>
</tr>
<tr>
<td>11×11</td>
<td>1×1×1</td>
<td>-0.18168</td>
<td>233.89082</td>
</tr>
</tbody>
</table>
(a) 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).

(b) Carbon 
Fluorine 
Bromine

(a) (b) (c) (d)

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 $Q_{Br_6}$ (e), and symmetrical stretching Br-Br frequencies $\omega_s$ (cm$^{-1}$) for the Br$_6$ over partially fluorinated graphene (see Fig. S3).

<table>
<thead>
<tr>
<th>$E_b$/Br (eV)</th>
<th>$Q_{Br_6}$ (e)</th>
<th>$\omega_s^b / \omega_a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) -0.359</td>
<td>-1.25</td>
<td>162.9 / 227.3</td>
</tr>
<tr>
<td>(b) -0.360</td>
<td>-1.28</td>
<td>159.6 / 225.2</td>
</tr>
<tr>
<td>(c) -0.359</td>
<td>-0.65</td>
<td>179.0 / 230.1</td>
</tr>
<tr>
<td>(d) -0.358</td>
<td>-0.59</td>
<td>181.9 / 231.1</td>
</tr>
</tbody>
</table>

**Fig. S4** Raman spectra taken at 514 nm for graphite intercalation compounds (C$_2$F$_x$-Br) synthesized without additional treatment with Br$_2$ vapors.