Electronic Supplementary Material (ESI) for Chemical Science.

SUPPLEMENTARY INFORMATION

Brominated graphene as a versatile precursor for multifunctional grafting

Heather Au, Noelia Rubio and Milo S. P. Shaffer*
Department of Chemistry, Imperial College London, London SW7 2AZ, UK.
*m.shaffer@imperial.ac.uk

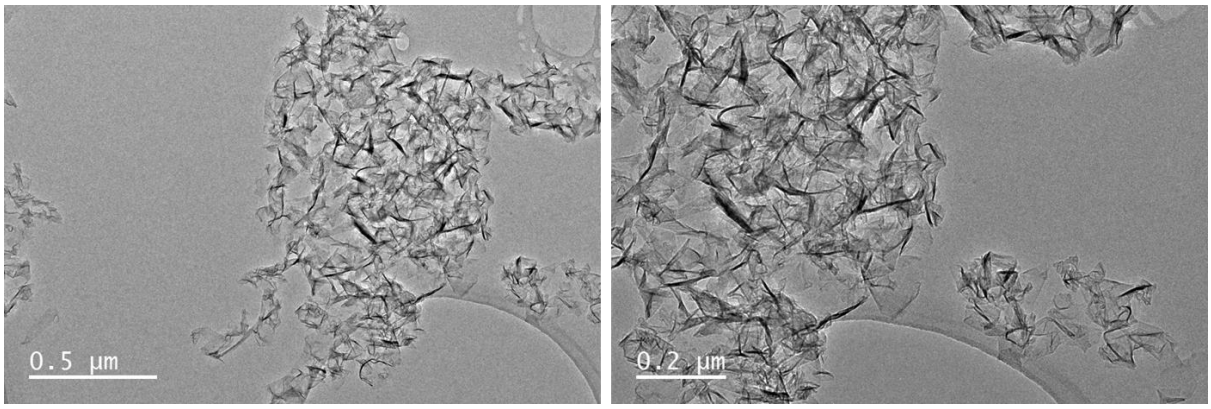

Figure S1. TEM images of as-received few-layer graphene deposited onto holey carbon film from ethanol solution. The flakes have a small lateral size and are slightly crumpled.

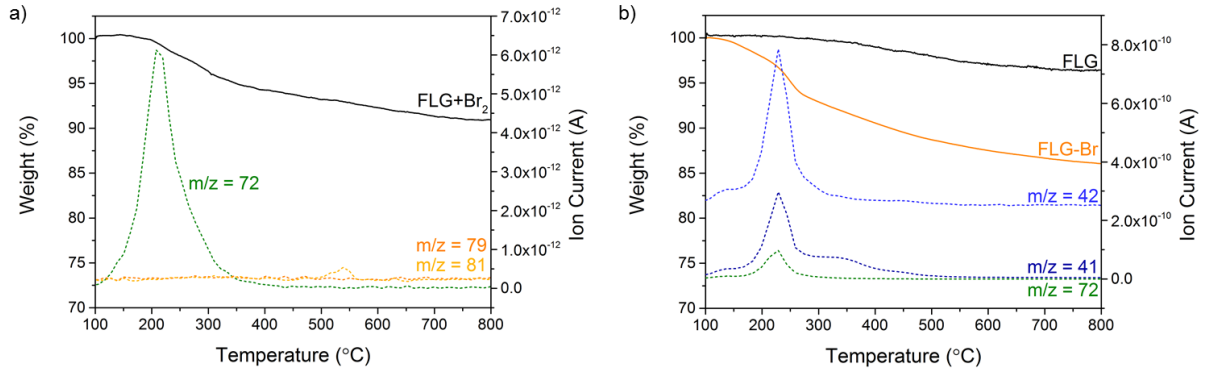

Figure S2. TGA-MS profiles of a) FLG+Br_2, *m/z* 72 THF; 79, 81 $–Br^+$; b) FLG-Br, *m/z* 41, 42, 72 THF. Due to the layered structure of few-layer graphene, solvent from the intercalation procedure can easily be trapped within the graphene layers and can only be removed at temperatures much higher than the solvent's boiling point, as seen in natural flake graphite.[1] In this case, THF remains in the sample, even in the bromine adsorption control. Since this amount of solvent may depend on the heterogeneity of the starting material, and the size of the grafted moiety, it is not straightforward to calculate the relative contribution to TGA mass loss. The calculations below ascribe the total mass loss to the grafted moiety alone, and should therefore be taken as an upper bound to the degree of grafting.

Determination of grafting data from TGA and XPS:

	Temperature range (°C)	%wt loss	End wt%*
FLG	100-800	3.6	96.4
FLG-Br	200-450	8.4	89.5
FLG-PMMA	200-550	16.2	83.0
FLG-PEG	300-500	18.7	78.6
FLG-OH	200-450	6.1	93.4

*Taken at the upper temperature of the range given in the table.

The **grafting ratio (GR)** is the mass fraction of grafted material, R, relative to the carbon framework, C, and can be deduced by taking the weight loss in the temperature range corresponding to the relevant *m/z* peaks, relative to the weight loss in as-received FLG, as the total amount of grafted material, ($wt\%_R$, assuming no residue after pyrolysis) and the residual weight as remaining FLG ($wt\%_C$):

$$GR = \frac{wt\%_R}{wt\%_C} \times 100$$

The **C/R ratio** (the number of FLG carbons per grafted moiety) for FLG-Br and FLG-PEG is calculated from:

$$C/R = \frac{MW_R}{wt\%_R} \times \frac{wt\%_C}{A_{rC}}$$

where MW_R and A_{rC} are the molecular weight of the grafted moiety and the atomic weight of carbon, respectively.

By XPS, C/Br for FLG-Br may be straightforwardly determined from atomic composition data. The grafting ratio is obtained using:

$$GR = \frac{A_{rBr}}{A_{rC}} \times \frac{1}{C/Br} \times 100$$

Calculation of number density (TGA and XPS):

The area of the graphene lattice per grafted moiety, $area_R(nm^2)$, is given by:

$$area_R(nm^2) = C/R \times area_C$$

Where $area_C$ is that occupied by one carbon in the lattice. Graphene's unit cell contains two carbon atoms and has an area of 0.0524 nm^2; therefore, the area occupied by one carbon atom is 0.0262 nm^2.

The number density of grafting per cm^2, n_D, is obtained using the relation:

$$n_D\ (cm^{-2}) = \frac{10^{14}}{area_R}$$

Determination of PMMA molecular weight and grafting ratio:

From the XPS data, approximately half (0.45) bromine addends serve as initiators, resulting in C/PMMA = 249 (using C/Br value obtained from XPS). The molecular weight can then be deduced using:

$$MW_{PMMA} = C/PMMA \times A_{rC} \times GR/100$$

resulting in a value of 590. Taking these proposed C/PMMA and M_n values of 249 and 590, respectively, for each polymer (containing 29.5 C and 11.8 O) there are 249 C and 8.9 O in the FLG framework (O/C ratio obtained from FLG starting material). These values can be used to predict atomic composition by dividing the sum for each element by the total atomic mass.

	Actual	Predicted
at% C	92.6	92.7
at% O	6.9	6.8
at% Br	0.5	0.4

The atom percents for each element can then be multiplied by the relevant atomic weight to obtain relative masses, which can then be used to calculate grafting ratio:

$$GR = \frac{at\%\ C_{PMMA} \times A_{rC} + at\%\ O_{PMMA} \times A_{rO}}{at\%\ C_{FLG} \times A_{rC}} \times 100$$

	TGA	XPS
GR	19.5	21.4

Calculation of FLG-PEG degree of substitution:

Degree of substitution can be calculated by:

$$degree\ of\ substitution = \frac{C/PEG}{C/Br}$$

where C/PEG is obtained from the TGA weight loss (disregarding bromine content) and has a value of 698.6.

For each PEG chain (containing 90 C and 45 O) there are 698.6 C and 25.7 O in the FLG framework. As before, these values are used to predict atomic composition and GR:

	Actual	Predicted
at% C	90.9	91.2
at% O	9.0	8.2
at% Br	0.1	0.6

	TGA	XPS
GR	23.8	26.2

Calculation of FLG-OH degree of substitution:

From XPS data, just over half (0.52) bromine addends were substituted by OH. The TGA weight loss for FLG-Br is 8.366% so:

$$wt\%_{OH} = 0.52 \times wt\%_{Br} \times \frac{MW_{OH}}{A_{rBr}}$$

Resulting in a weight loss from OH addends of 0.93%. Summing the contributions from Br and OH and dividing by the new total (wt%OH + wt%Br + wt%C) results in a predicted TGA weight loss of 5.6% and a carbon weight of 94.4%, similar to actual values of 6.1% and 93.4%.

The C/OH ratio is 163 giving a GR of 3.8.

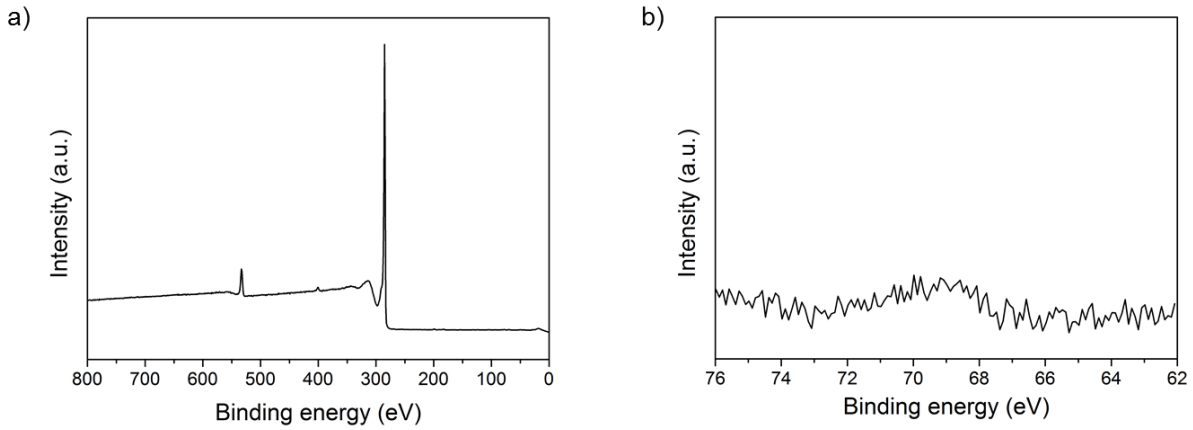

Figure S3. a) Wide survey XPS spectrum, and b) core level Br 3d spectrum for FLG+Br_2. Compositional values obtained by XPS (95.4 at% C, 4.5 at% O, 0.1 at% Br) show that most of the adsorbed bromine may be removed by washing, whilst the slight increase in O/C compared to the starting material suggests that a small amount of THF remains trapped.

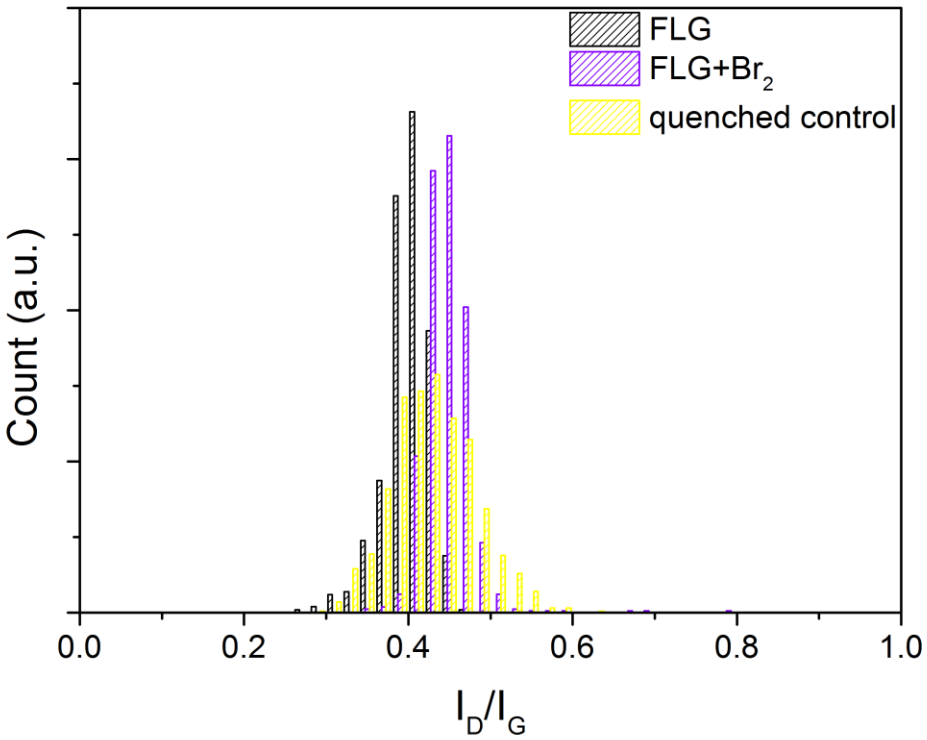

Figure S4. Raman histograms of I_D/I_G ratio of FLG (black), FLG+Br_2 (purple) and quenched control (yellow); λ_{exc} = 532 nm. The I_D/I_G ratios for FLG+Br_2 (0.45) and the quenched control (0.43) increase only slightly compared to FLG starting material, suggesting that no functionalisation occurs by either process.

Table S1. Summary of Raman data* for functionalised FLGs, λ_{exc} = 532 nm.

	I_D/I_G	$I_D/I_{D'}$	I_{2D}/I_G	Γ_D (cm^{-1})	Γ_G (cm^{-1})	Γ_{2D} (cm^{-1})	2D peak position (cm^{-1})
FLG	0.40 ± 0.03	3.0 ± 0.6	0.97 ± 0.04	53 ± 6	32 ± 2	58 ± 1	2694.3 ± 0.6
FLG-Br	0.58 ± 0.02	3.9 ± 0.4	1.02 ± 0.05	43 ± 7	30 ± 5	55 ± 2	2694.0 ± 2.2
FLG-PMMA	0.53 ± 0.03	4.0 ± 0.6	1.06 ± 0.05	43 ± 4	29 ± 1	53 ± 1	2691.1 ± 1.0
FLG-PEG	0.56 ± 0.03	3.9 ± 0.6	1.02 ± 0.04	43 ± 4	30 ± 1	55 ± 2	2693.6 ± 0.7
FLG-OH	0.57 ± 0.09	4.0 ± 1.3	0.99 ± 0.04	44 ± 3	30 ± 1	56 ± 3	2693.8 ± 0.6

Mean values and standard deviation calculated from at least 500 spectra.

FLG and its functionalised derivatives show well-defined D, G and 2D peaks, although the full width at half maximum (Γ) values for the D and G bands are wider than those quoted in the literature for graphitic carbon with a low density of defects (typically Γ_D<30 cm^{-1} and Γ_G<14 cm^{-1}).[2, 3] Line broadening occurs in these FLG materials likely due to edge effects and surface oxides, and the crumpled nature of the sheets.

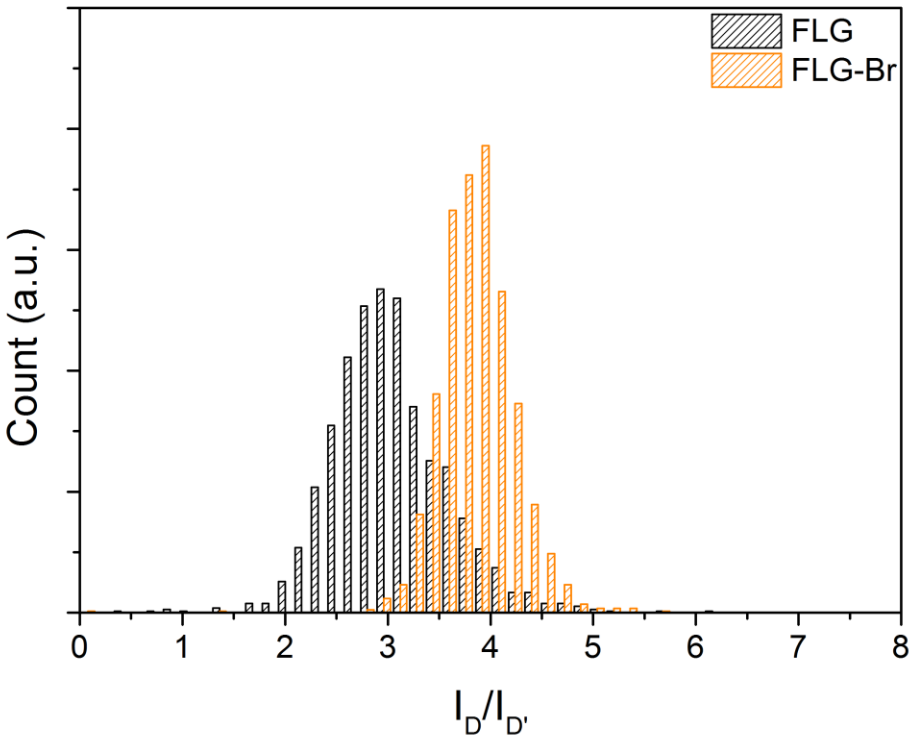

Figure S5. Raman histograms of $I_D/I_{D'}$ ratio of FLG (black) and FLG-Br (orange); λ_{exc} = 532 nm.

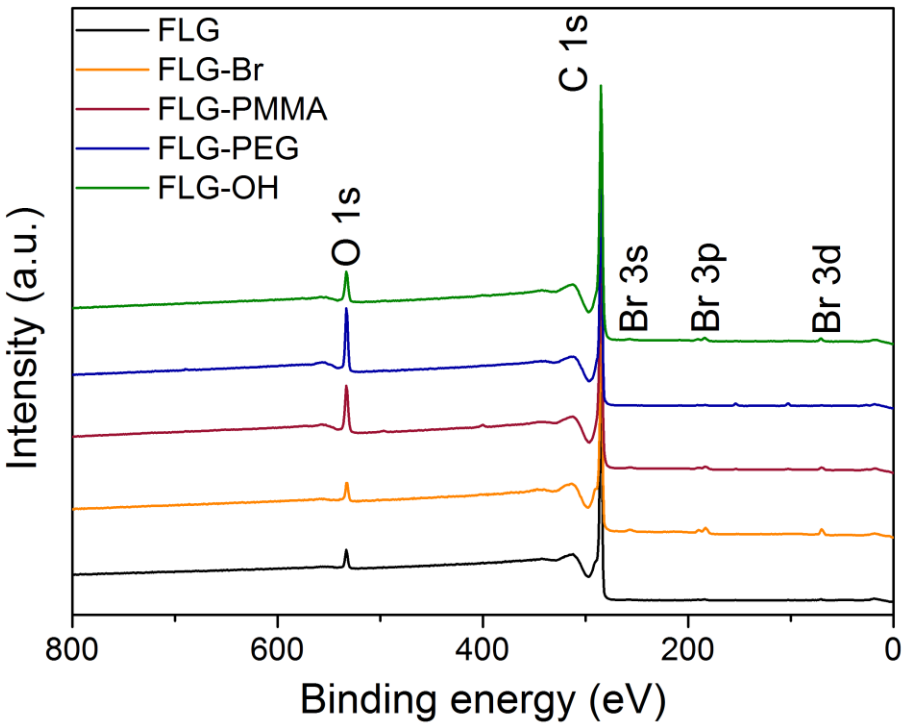

Figure S6. Wide survey XPS spectra of FLG (black), FLG-Br (orange), FLG-PMMA (red), FLG-PEG (blue) and FLG-OH (green). The increase in the O1s peak for FLG-PMMA, FLG-PEG and FLG-OH is consistent with subsequent grafting reactions.

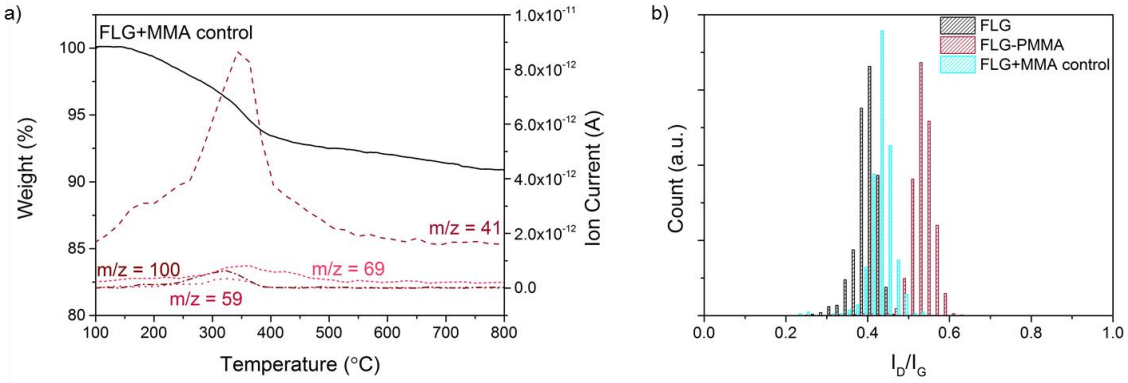

Figure S7. a) TGA-MS profile and b) Raman histograms of I_D/I_G ratio of FLG+MMA control; λ_{exc} = 532 nm. TGA-MS shows a small weight loss which may be attributed to residual THF trapped between the graphene layers. The fragment *m/z* 41 is common to both PMMA and THF; since the mass spectrum shows no other fragments corresponding to PMMA, this particular *m/z* peak may be attributed to THF. In the Raman spectra, the I_D/I_G ratio (0.43) increases only slightly compared to FLG starting material, suggesting that no functionalisation has taken place, and therefore that bromine sites are required to initiate polymerisation.

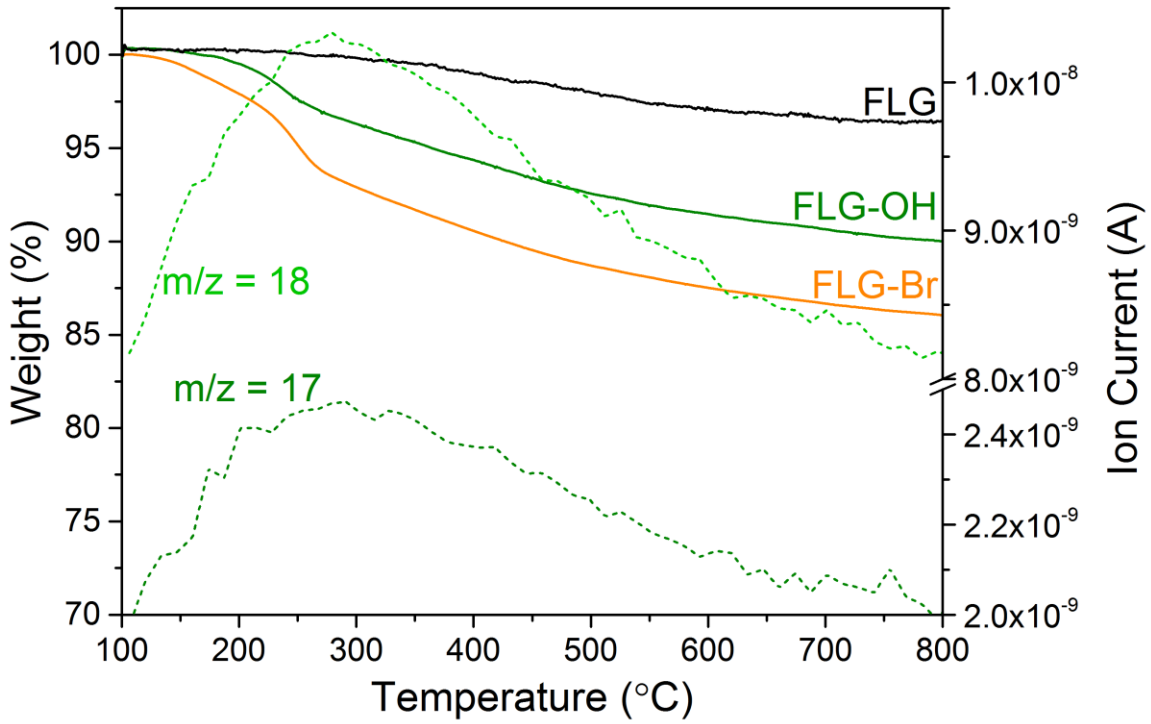

Figure S8. TGA-MS profile of FLG-OH, *m/z* 17 ($-OH^+$) and 18 (H_2O^+).

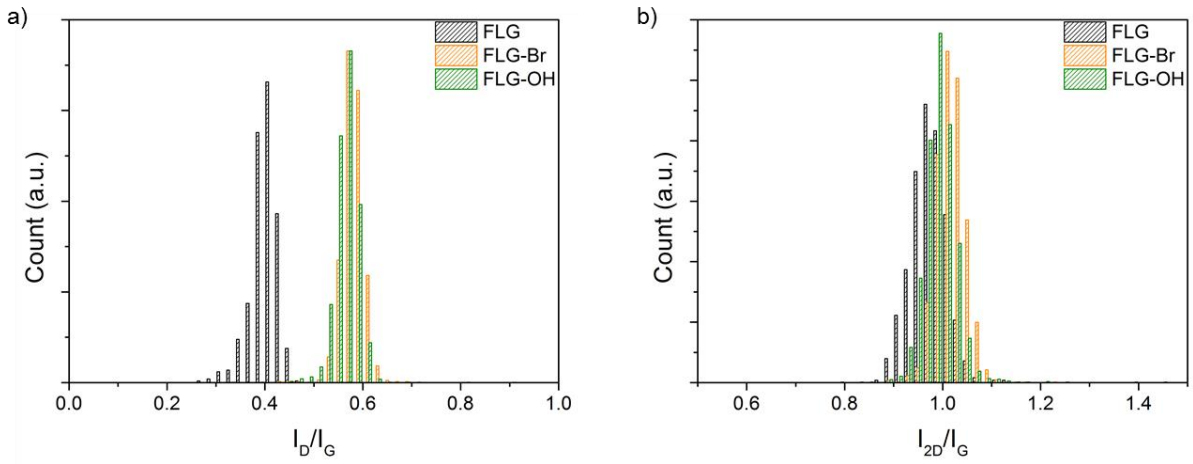

Figure S9. Raman histograms of a) I_D/I_G ratio and b) I_{2D}/I_G ratio of FLG (black), FLG-Br (orange) and FLG-OH (green); λ_{exc} = 532 nm.

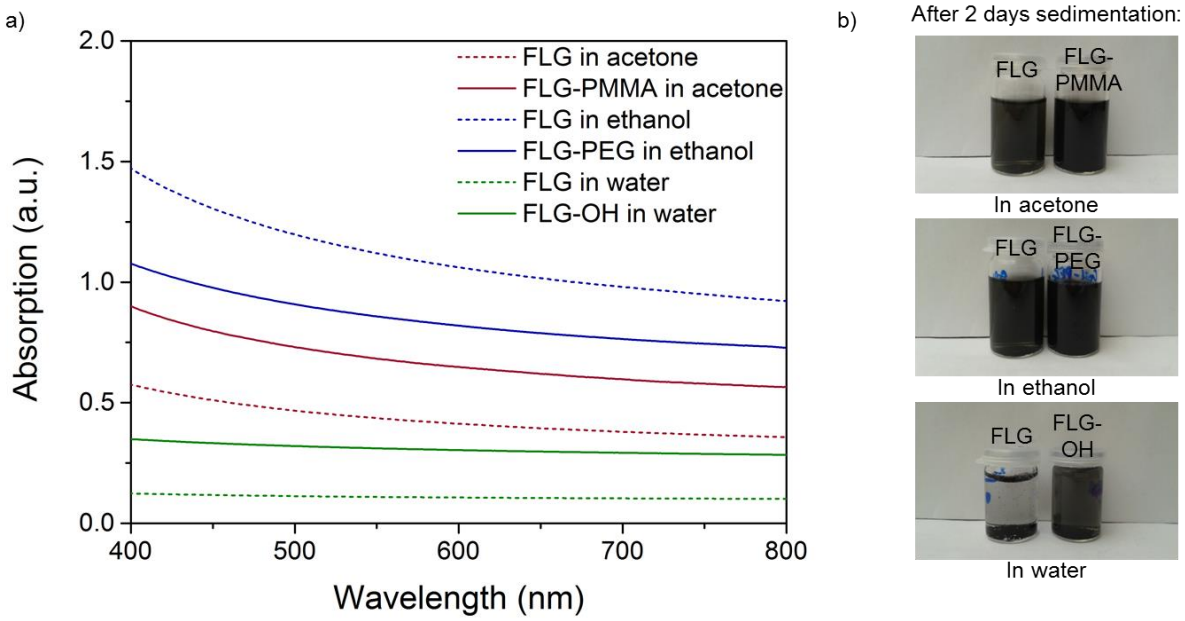

Figure S10. a) UV-vis spectra of functionalised FLGs in acetone, ethanol and water. Supernatants were taken after 2 days sedimentation. For measurement, FLG samples were diluted 2× and functionalised FLGs 8×; spectra values have been multiplied accordingly. b) Photographs of the supernatant solutions of functionalised FLGs.

Table S2. Calculated concentrations of functionalised FLGs obtained from UV/vis absorption spectra.

	Solvent	**Concentration (µg mL^{-1})**
FLG	acetone	31.8
FLG-PMMA	acetone	200
FLG	ethanol	82.0
FLG-PEG	ethanol	255
FLG	water	8.51
FLG-OH	water	96.4

The absorption at 660 nm and the extinction coefficient for dispersed graphene in solution (α_{660} = 2460 L g^{-1} m^{-1})^4 were used to estimate the concentrations of the different solutions using the Beer-Lambert law.

References

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