Supplementary Information

Understanding and Controlling the Covalent Functionalisation of Graphene

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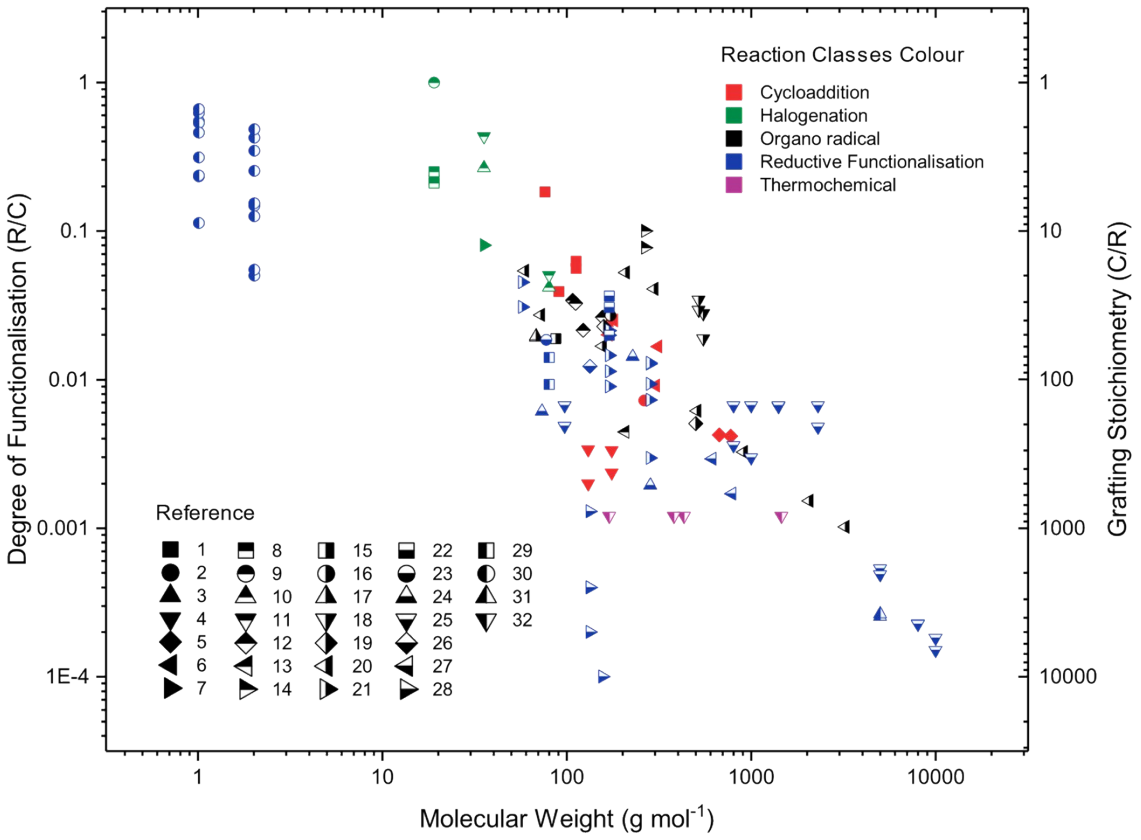

Figure S1. Fully annotated version of Figure 2b in the main text; Degree of functionalisation for reactions with the graphene carbon framework: summary of available literature plotting molecular weight of grafted moiety versus degree of functionalisation (R/C, left) and grafting stoichiometry (C/R, right), categorised by reaction type (by colour), annotating each data point with its respective reference.

Table S1. Tabulated summary of available literature data used in Figures 2b and S1 of various graphene-functionalisation reaction types, describing molecular weights of the grafted moieties and the grafting stoichiometry, as determined by either TGA or XPS, with corresponding references.

Reaction Class	Mw(R) (g/mol)	C/R (TGA)	C/R (XPS)	Reference
Cycloaddition	76.1	5.4		1
	112.08	17.8	16.0	
	90.13	25.5		
	262.4	137.7		2
	165.21	41.3		3
	130.18	296.3		4
	130.18	501.1		
	175.18	423.8		
	175.18	299.9		
	667.81	235.0		5
	772.21	240.0		
	179.19		40.0	6
	167.6		50.0	
	303.49		110.0	
	311.37		60.0	
Halogenation	35.45		12.5	7
	19		4.0	8
	19		4.6	
	19		4.8	
	19		1.0	9
	35.45		3.8	10
	79.9		24.0	
	35.45		2.3	11
	79.9		19.8	
Organo radical	111.55	30.6		12
	122.11	46.6		
	107.14	29.3		
	156	38.0		
	207.21	224.5		13
	266.33	10.0	13.0	14
	87.22		53.0	15
	171.81	37.0		16
	68.11	51.1	52.0	17
	547.16	35.8	53.0	18
	519.1	34.0	29.0	
	158.17	44.0		19
	498.7	198.0		
	59.08	18.6		20
	72.13	36.9		
	208.07	19.1		
	156.16	59.6		
	297.45	24.6		
	3225.17	980.0		
	507.19	163.0		
	907.19	307.0		
	2057.19	655.0		
Reductive Functionalisation	57.13	32.4		21
	169.37	111.1		
	169.37	88.1		
	169.37	68.9		
	281.61	337.5		
	281.61	137.2		
	57.13	22.1		

Reaction Class	Mw(R) (g/mol)	C/R (TGA)	C/R (XPS)	Reference
Reductive Functionalisation	169.37	46.8		21
	281.61	78.5		
	281.61	107.1		
	281.61	77.2		
	169.37	50.3		22
	169.37	27.5		
	169.37	32.8		
	77.11	54.2		23
	73.21	163.4		24
	283.66	513.6		
	227.54	70.1		
	800	149.0	278.0	25
	1000	149.0	334.0	
	1400	149.0	151.0	
	2300	149.0	208.0	
	5000	2055.0	1869.0	
	8000	4421.0	4390.0	
	10000	6615.0	5490.0	
	97.02	206.0	149.0	
	133.23	81.4		26
	613.77	342.3		27
	782.13	586.6		
	133.23	2500		28
	156	10000		
	133.23	769.0		
	133.23	2500		
	133.23	5000		
	79.9	71.0	108.0	29
	1.01	2.2		30
	1.01	1.5		
	1.01	1.6		
	1.01	3.2		
	1.01	1.9		
	1.01	1.8		
	1.01	4.2		
	1.01	8.8		
	1.01	4.3		
	2.01	6.5		
	2.01	2.1		
	2.01	2.4		
	2.01	6.8		
	2.01	2.9		
	2.01	3.9		
	2.01	7.9		
	2.01	20.0		
	2.01	18.2		
	5000	3924.0		31
	5000	3792.0		
Thermochemical	169.3	830.0		32
	380.38	830.0		
	430.91	830.0		
	1452.08	830.0		
Oxidation				33
Oxidation				34

When interpreting data in the literature, the following relationships were used determine C/R:

$$\frac{C}{R} = \frac{wt\%(C)}{Ar(C)} \times \frac{Mw(R)}{wt\%(R)} \quad \text{(S1)}$$

Used for TGA data where wt%(R) and wt%(C) are the weight percentages of the functional group and framework carbon (usually the remaining mass after pyrolysis), respectively; Mw(R) and Ar(C) are the molecular and atomic weights of the functional group and carbon respectively.

$$\frac{C}{R} = \frac{at\%(C) - \frac{at\%(X) \times n}{m}}{\frac{at\%(X)}{m}} \quad \text{(S2)}$$

For XPS data, for functional groups with carbon to heteroatom (X) stoichiometry ${}_{C_n}X_m$, with at%(C) and at%(X) the atomic percentages of carbon and heteroatom respectively.

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