Supporting Information

Functionalization of Graphene by Electrophilic Alkylation of Reduced Graphite

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Experimental Details:

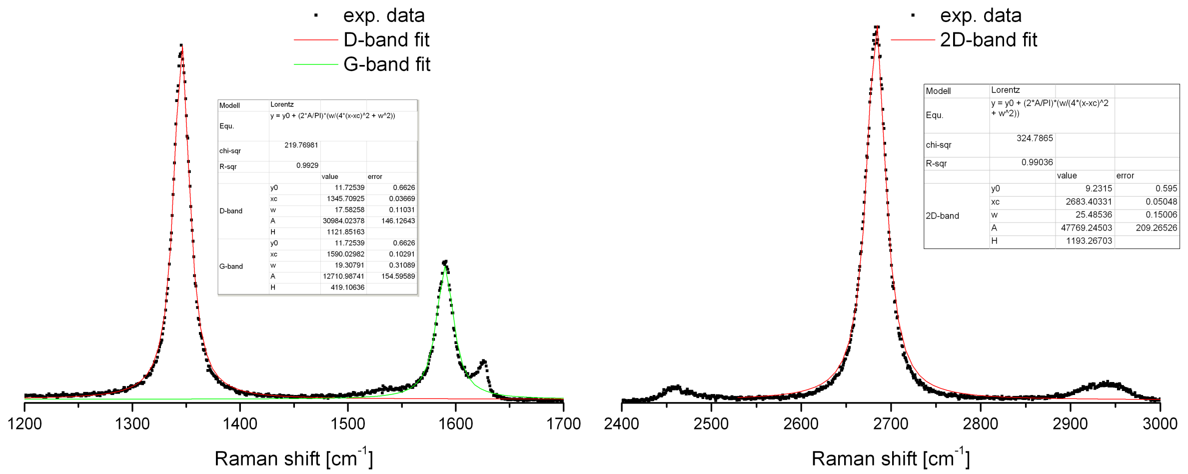
Instrumentation:

Raman spectroscopy was carried out on a Horiba Jobin Yvon LabRAM Aramis at 532 nm excitation wavelength equipped with a motorized sample holder. TGA/MS analysis was carried out on a Netzsch STA 409 CD on a 10K/min temperature ramp using Helium as inert gas. Absorbance measurements were conducted on a Perkin Elmer Lambda 1050 in 1 cm path length suprasil cuvetts. HRTEM measurements were conducted on a Titan^3 80-300 microscope operating at 80 kV electron acceleration voltage from dropcasted and centrifuged graphene dispersions obtained by bath-ultrasonication in isopropanol.

Preparation:

150 mL freshly distilled dry 1,2-DME were filled into a flame dried argon filled round bottom flask. 1.01 mL NaK-alloy (17.7 mmol K/ 8.3 mmol Na based on eutectical composition) were transferred into the flask and stirred until the dissolution of the metal forms a deep blue solution. Into this solution 24 mg (2.0 mmol carbon) natural graphite flakes (Kropfmühl AG, Passau) were added and stirred for 7 days before 3.0 mL (20 mmol, 10 eq.) 1-iodohexane (Sigma Aldrich) was injected *via* a syringe. The reaction mixture was stirred for another 7-days before spincasting of samples and workup. After addition of 150 mL cyclohexane, the organic layer was washed with 600 mL water, homogenized with 20 mL of ethanol and filtered through 0.2 µm regenerated cellulose membranes. The filtercake was washed with 20 mL of cyclohexane, tetrahydrofuran, isopropylalcohol, ethanol, methanol and water and subsequently redispersed in THF to hinder reaggregation. Samples for TGA/MS and Raman spectroscopy were filtered again and dried at 70°C *in vacuo* prior to analysis. Absorbance samples were prepared after filtration by stirring but without drying in vacuum in order to reduce the degree of aggregation.

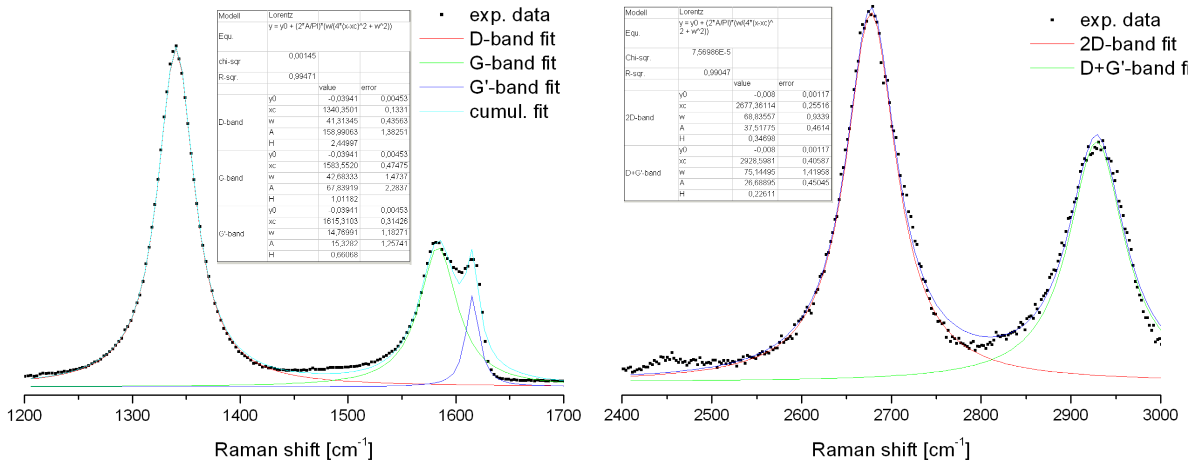
Figure S1: Raman spectrum of hexylated graphene and results as discussed in the main text



Modell	Lorentz		
Equ.	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
chi-sqr	219.76981		
R-sqr	0.9929		
		value	error
D-band	y0	11.72539	0.6626
	xc	1345.70925	0.03669
	w	17.58258	0.11031
	A	30984.02378	146.12643
	H	1121.85163	
G-band	y0	11.72539	0.6626
	xc	1590.02982	0.10291
	w	19.30791	0.31089
	A	12710.98741	154.59589
	H	419.10636	

Modell	Lorentz		
Equ.	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
chi-sqr	324.7865		
R-sqr	0.99036		
		value	error
2D-band	y0	9.2315	0.595
	xc	2683.40331	0.05048
	w	25.48536	0.15006
	A	47769.24503	209.26526
	H	1193.26703	

Typical Raman spectrum with L_D = 6.1 nm and I(D)/I(G) = 2.67

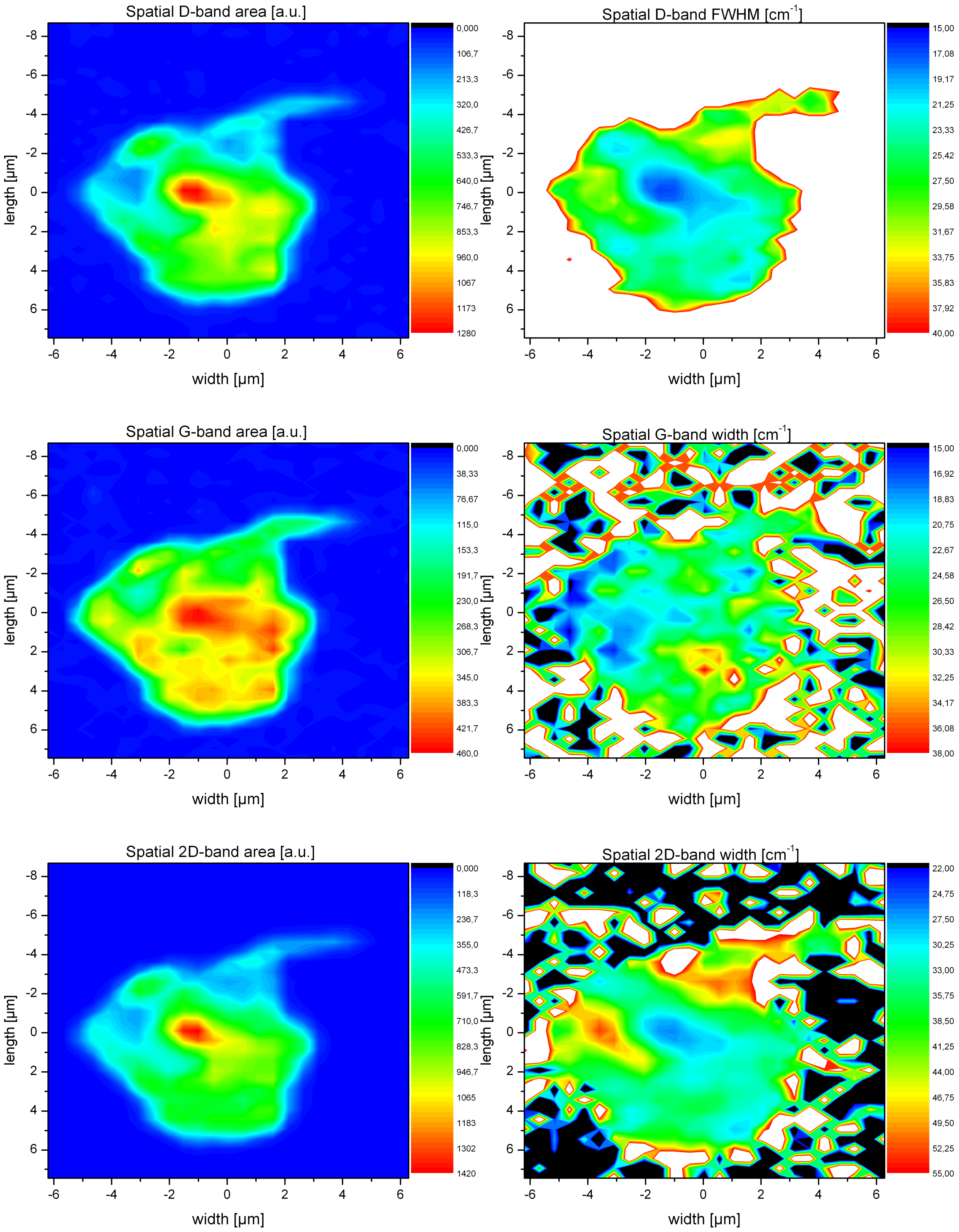


Modell	Lorentz		
Equ.	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
chi-sqr	0,00145		
R-sqr.	0,99471		
		value	error
D-band	y0	-0,03941	0,00453
	xc	1340,3501	0,1331
	w	41,31345	0,43563
	A	158,99063	1,38251
	H	2,44997	
G-band	y0	-0,03941	0,00453
	xc	1583,5520	0,47475
	w	42,68333	1,4737
	A	67,83919	2,2837
	H	1,01182	
G'-band	y0	-0,03941	0,00453
	xc	1615,3103	0,31426
	w	14,76991	1,18271
	A	15,3282	1,25741
	H	0,66068	

Modell	Lorentz		
Equ.	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
Chi-sqr.	7,56986E-5		
R-sqr.	0,99047		
		value	error
2D-band	y0	-0,008	0,00117
	xc	2677,36114	0,25516
	w	68,83557	0,9339
	A	37,51775	0,4614
	H	0,34698	
D+G'-band	y0	-0,008	0,00117
	xc	2928,5981	0,40587
	w	75,14495	1,41958
	A	26,68895	0,45045
	H	0,22611	

Exemplary Raman spectrum with L_D = 1.85 nm and I(D)/I(G) = 2.45

S2: Spatially resolved Raman spectroscopy of a hexylated graphene flake – Area vs. FWHM



S3: Spatially resolved Raman spectroscopy of a hexylated graphene Flake – Area vs. Peak Position

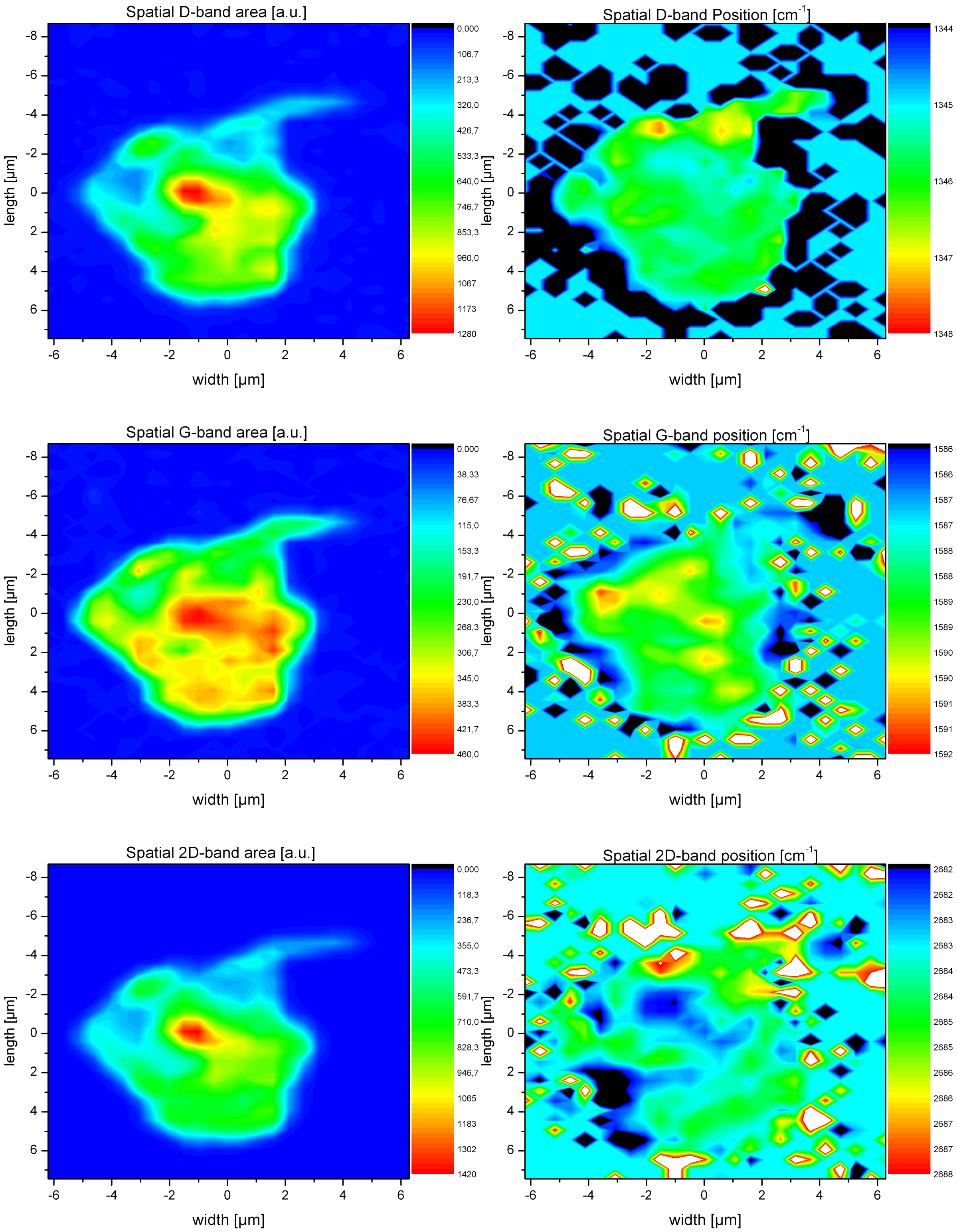
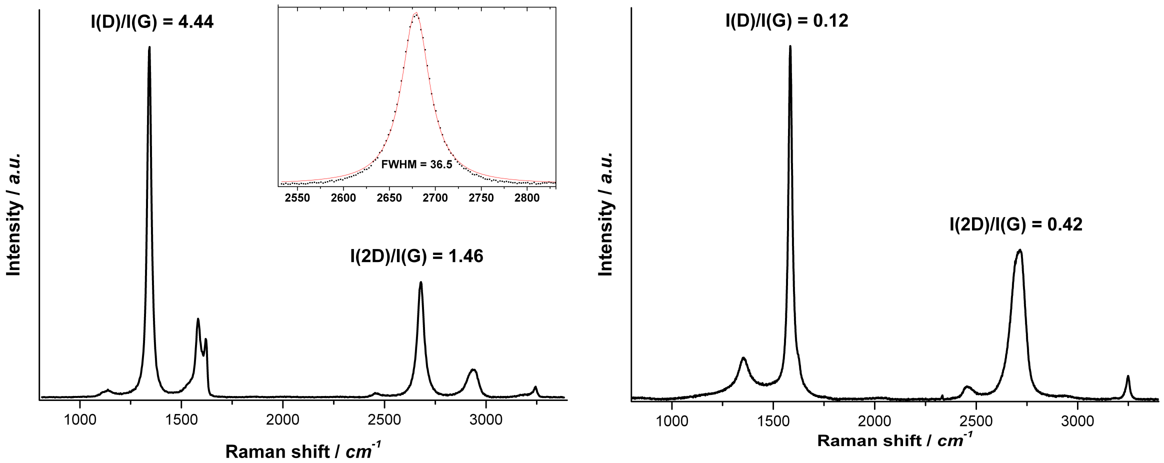


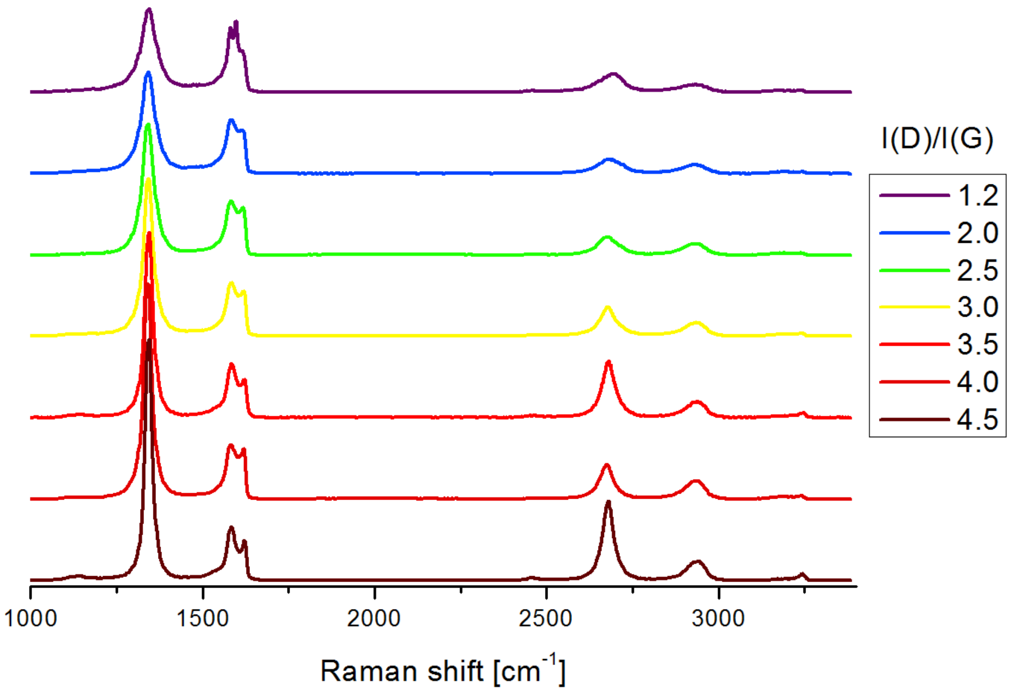
Figure S4: Raman spectrum of a hexylated graphene flake before and after TGA



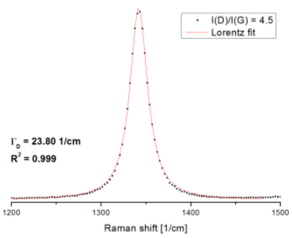
(left): Raman spectrum of highly functionalized single layer graphene recorded directly from the cellulose filter after filtration at $\lambda_{\text{exc.}}$ = 532 nm. I(D)/I(G) ratios of up to 4.44 were measured on a large area survey. I(2D)/I(G) ratio is slightly decreased compared to lower functionlized materials accompanied by a broadening of the lorentzian 2D-band to FWHM values of 36.5 cm^{-1}.

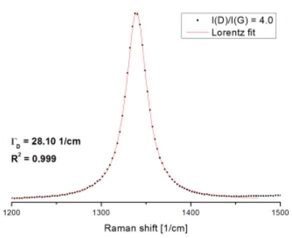
(right): Raman spectrum after TGA (thermal annealing to 1000°C in helium atmosphere). A substantial decrease in I(D)/I(G) ratio to 0.12 is found accompanied with reaggregation as seen in the asymmetrical lineshape of the 2D-band that needed to be fitted by a minimum of two Lorentz functions.

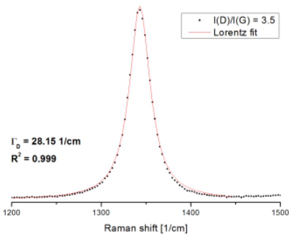
Figure S6: Series of Raman spectra with increasing functional group density (bottom to top)

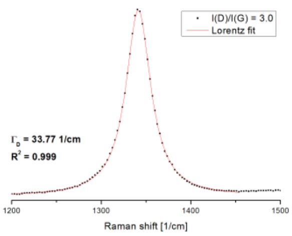


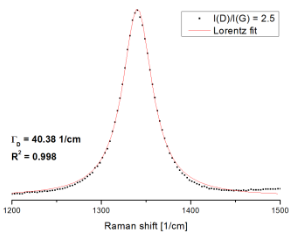
Raman spectra extracted from a large area scan obtained on filtered material after functionalization. In order to quantify the amount of defects conveniently, L_D, the distance between two point defects, is to be discussed. The broad range of I(D)/I(G) ratios recorded from the sample reflects the steep interval of the I(D)/I(G) vs. L_D curve for L_D = 2-5 nm and thus very high functionalization. I(D)/I(G) in our case reaches its maximum at 4.5 which reflects a L_D of approx. 3 nm and then decreases down to a minimum of I(D)/I(G) = 1.2 with increasing functional group density and thus lower L_D [*Nano Lett.* **2011**, *11*, 3190]. To further corroborate this finding and to exclude the possibility of decreasing L_D with decreasing I(D)/I(G) additionally the half-width Γ_D of the D band was fitted for various I(D)/I(G) ratios as spectral broadening is only to be expected in the range of low L_D (2-5 nm).











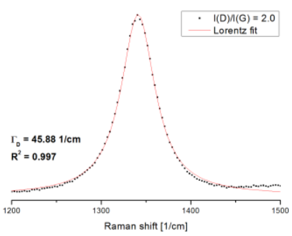
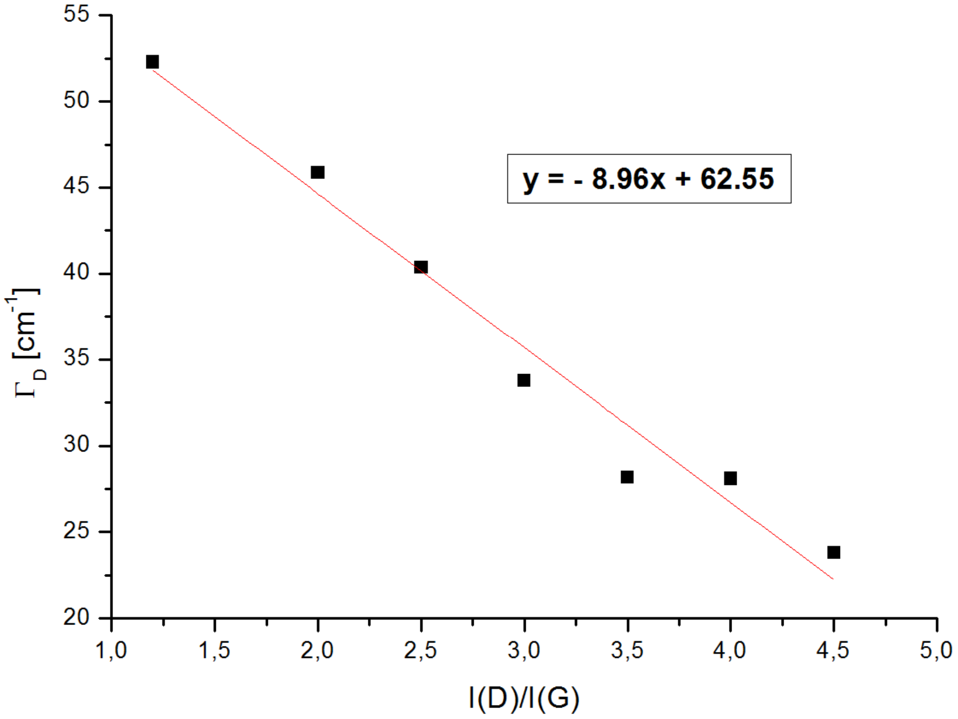
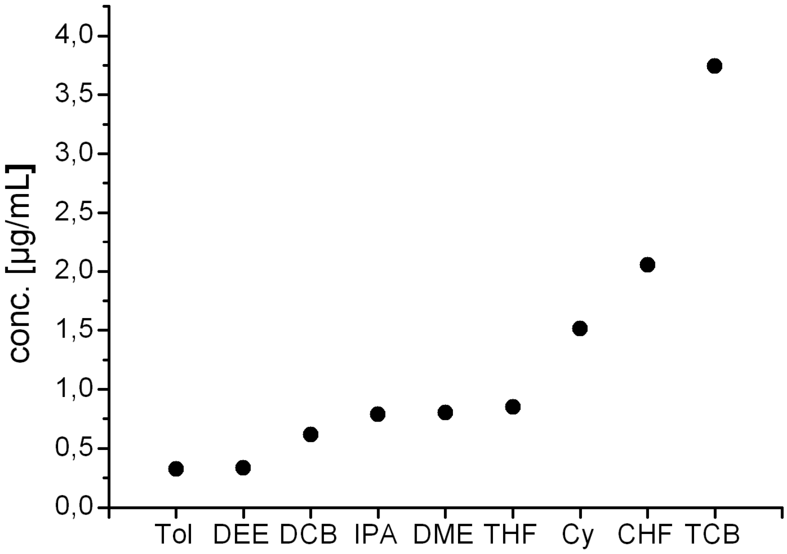


Figure S7: Linear Correlation between the FWHM of the D-band and the I(D)/I(G) ratio



A clear linear dependence between the I(D)/I(G) ratio and the half width Γ_D of the D band is observed. The recorded broadening reflects the very high degree of functionalization and thus the low L_D values discussed before.

Figure S8: Absorption Spectroscopy



Solubility of functionalized graphene in the common organic solvents toluene (**Tol**), diethyl ether (**DEE**), *ortho*-dichlorobenzene (**DCB**), isopropyl alcohol (**IPA**), 1,2-dimethoxyethane (**DME**), tetrahydrofuran (**THF**), cyclohexane (**Cy**), chloroform (**CHF**) and 1,2,4-trichlorobenzene (**TCB**) determined by using the absorption coefficient for dispersed graphene published in [*Nat. Nanotechnol.* **2008**, *3*, 563].

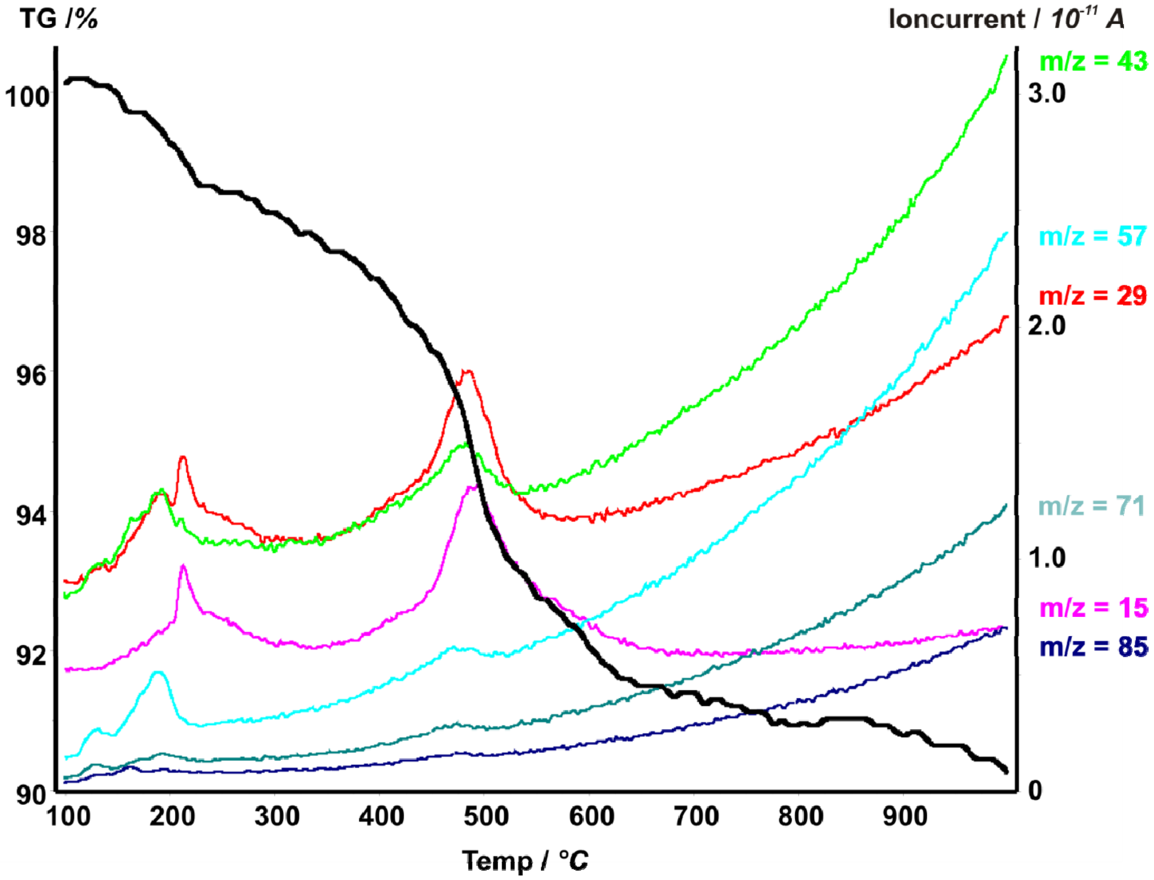
solvent	concentration [µg/mL] [a]
toluene	0.32
diethylether	0.33
o-dichlorobenzene	0.61
isopropanol	0.79
1,2-dimethoxyethane	0.80
tetrahydrofuran	0.85
cyclohexane	1.51
chloroform	2.05
1,2,4-trichlorobenzene	3.74

[a] conservative estimation based on the extinction coefficient published in ref.[*Nat. Nanotechnol.* **2008**, *3*, 563]

Table 1. Solubility of hexyl functionctionalized graphene

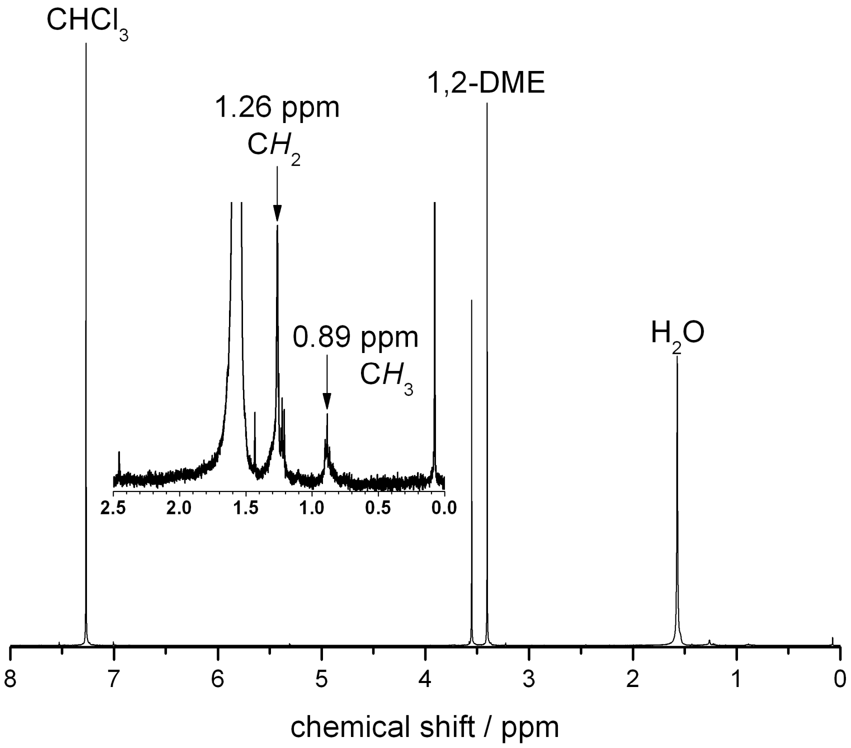
The hexylchain derivatized graphene material exhibits an increased solubility in broad variety of organic solvents with different polarities. To quantify this solubility 0.1 mg/mL were sedimented in toluene, cyclohexene, o-dichlorobenzene, 1,2,4-trichlorobenzene, chloroform, diethylether, 1,2-dimethoxyethane, tetrahydrofuran and isopropylalcohol followed by stirring at 500 rpm using a magnetic stirrer for 5 days without the need of ultrasonication. After mild centrifugation of these dispersions for 20 minutes at 500 rpm the absorbance of the clear supernatant solution was measured. The recorded spectra from chloroform and cyclohexane solutions, shown in figure 4, are chosen due to the solvents optical transparency in the deep UV spectral region. The spectra are featureless and monotonically increasing towards higher photon energies, except of a single band centered at ~276 nm. To quantify the graphene content in every solvent used, the extinction coefficient of graphene in organic solvents determined by Hernandez *et al.* of 24.6 mL mg^{-1} cm^{-1} at $\lambda = 660$ nm was used. [*Nat. Nanotechnol.* **2008**, *3*, 563] Based on this the concentrations vary from 0.32 µg/mL for toluene to 3.74 µg/mL in 1,2,4-trichlorobenzene which is in the same order of magnitude than ultrasound processed graphene in organic media. It needs to be mentioned though, that the introduction of sp^3 centers during the functionalization and thus the destruction of the conjugated π-electronic system reduced the absorption cross section in the visible light spectrum. Hence the given concentrations are to be regarded as the low water mark of a conservative estimation.

Figure S9: Thermogravimetric analysis (TGA) coupled with mass spectrometry



TGA-MS analysis of the covalently functionalized graphene. Two areas of defined massloss can be identified at ~200 °C and 490 °C and are attributed to physisorbed and chemisorbed functional groups. The colored graphs represent the ion currents as a function of temperature for methyl ($^m/_z$ 15), ethyl ($^m/_z$ 29), propyl ($^m/_z$ 43), butyl ($^m/_z$ 57), pentyl ($^m/_z$ 71 and hexyl ($^m/_z$ 85) cations.

Figure S10: Solution ^{1}H-NMR spectroscopy of hexylated material



400 MHz ^{1}H-NMR spectroscopic investigations of the material dispersed in $CDCl_3$ clearly displays signals for aliphatic CH_2 at 1.26 ppm and CH_3 at 0.89 ppm which is attributed to the presence of hexyl chains.