Supporting Information

Screening of Graphites – Potential Starting Materials for Functionalized Graphene

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Experimental Details:

Instrumentation:

Raman Spectroscopy

The Raman spectroscopic characterization was carried out on a HoribaLabRAM Aramis confocal Raman microscope ($\lambda_{exc.}$ = 532 nm) with a laser spot size of about 1 µm (Olympus LMPlanFl 100x, NA 0.80). The incident laser power was kept as low as possible to avoid structural sample damage: 240 µW (532 nm). Spectra were achieved by a CCD array at -70 °C and a 600 grooves/mm grating from a 100 µm x 100 µm area with 1 µm step size in SWIFT mode for low integration times. Sample movement was obtained by an automated XY-scanning table.

Thermogravimetric Analysis coupled with Mass Spectrometry (TGA/MS)

Mass spectrometer coupled thermogravimetric analysis (TGA/MS) was carried out on a Netzsch STA 409 CD instrument equipped with a Skimmer QMS 422 mass spectrometer (EI ion source, quadrupole mass spectrometer) with the following programmed time-dependent temperature profile: 24-100 °C (dynamic heating of 10 K/min), 100 °C for 30 min (isothermic heating step) and 100-800 °C (10 K/min temperature ramp).
The initial sample weights were about 5-10 mg, and the experiments were performed under inert gas atmosphere with a helium gas flow of 80 mL/min.

Infrared spectroscopy

BRUKER Tensor® 27 FT-IR spectrometer in transmission mode

UV/Vis absorption spectroscopy

PerkinElmer Lambda 1050 using precision cells made of Quartz SUPRASIL® (Hellma) with 10 mm light path

Scanning Electron Microscopy

Large chamber SEM, Institute of Advanced Materials and Processes, University of Erlangen-Nürnberg

Preparation:

Under an argon atmosphere 0.45 mL of a freshly prepared, liquid Na/K alloy (3.9 mmol Na and 7.7 mmol K for an eutectic mixture) in 150 mL dry 1,2-DME (freshly distilled over Na/K) were stirred in a flame dried round bottom flask at room temperature. 24 mg (2.0 mmol carbon) of graphite was added to the deep-blue solution and the dispersion was stirred for three days. Afterwards, 4.9 mL (5.92 g, 20 mmol, 10 eq.) of dodecyl iodide (Sigma Aldrich) was injected, after a short ultrasonic pulse. The reaction mixture was stirred overnight and treated with 50 mL cyclohexane and 50 mL distilled water for workup. After washing of the carbon material with distilled water (overall 200 mL) for three times, the organic layer containing the product was filtered through a 0.2 µm reinforced cellulose membrane filter (Sartorius) and washed with THF, isopropanol and distilled water (50 ml each), to remove salts and excess reagent. In a vacuum oven at 70 °C the resulting solid was dried overnight.

Starting materials:

G(flake): natural passau *(Kropfmühl AG, Passau)*

G(powder): PEX10 *(Future Carbon 2010)*

G(spherical): SGN18 *(Future Carbon 2010)*

Table S1: Graphite data (according to manufacturer)

Type	Description	Grain (in µm)	C (in %)	A (in m^2/g)	pH
G(flake*)†	natural flake	1000‡ (**18**†)	-	0.2	7.33
G(powder)	intercal. (H_2SO_4), expanded and delaminated	3-5	98.5	6	6.02
G(spherical)	natural spherical	20	99.99	6.2	7.12

† pre-treatment of natural graphite as starting material:

natural graphite flakes (Kropfmühl AG, Passau) are comminuted with 5 times the amount of sodium chloride in a mortar for 20 min, whereby, after the elution of NaCl with distilled water and drying in vacuum, smaller and easier dispersible graphite flakes are achieved than in the case of the original natural graphite flakes

→ G(flake): determined grain ca. 18 µm

‡ Supporting Information; J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H.-P. Steinrück, E. Spiecker, F. Hauke and A. Hirsch, *Nat. Chem.*, 2011, **3**, 279-286.

Table S2: Graphite data (determined)

Type	d_{bulk} (in mg/cm^3)	Raman $(I_D/I_G)_{average}$	TGA/MS mass loss (in %)
G(flake)	400	0.2	-0.3
G(powder)	90	0.3	-2.4
G(spherical)	270	0.4	-0.7

Table S3: Raman-data of dodecyl-functionalized graphene samples, using different types of graphite as starting material

Type	Raman $(I_D/I_G)_{average}$	mean defect distance (in nm)	approx. framework atoms per addend
$C_{12}H_{25}$-G(flake)	1.9	8	2,200
$C_{12}H_{25}$-G(powder)	3.1	5	850
$C_{12}H_{25}$-G(spherical)	2.5	6	1,200

Table S4: Determined data of the starting graphites and the dodecyl-functionalized materials

Type	Grain (in µm)	Conductivity σ (in S/cm)
G(flake)	18	1200
G(powder)	4	298
G(spherical)	20	538

Type	Grain (in µm)	Conductivity σ (in S/cm)
$C_{12}H_{25}$-G(flake)	89	32
$C_{12}H_{25}$-G(powder)	72	9
$C_{12}H_{25}$-G(spherical)	91	17

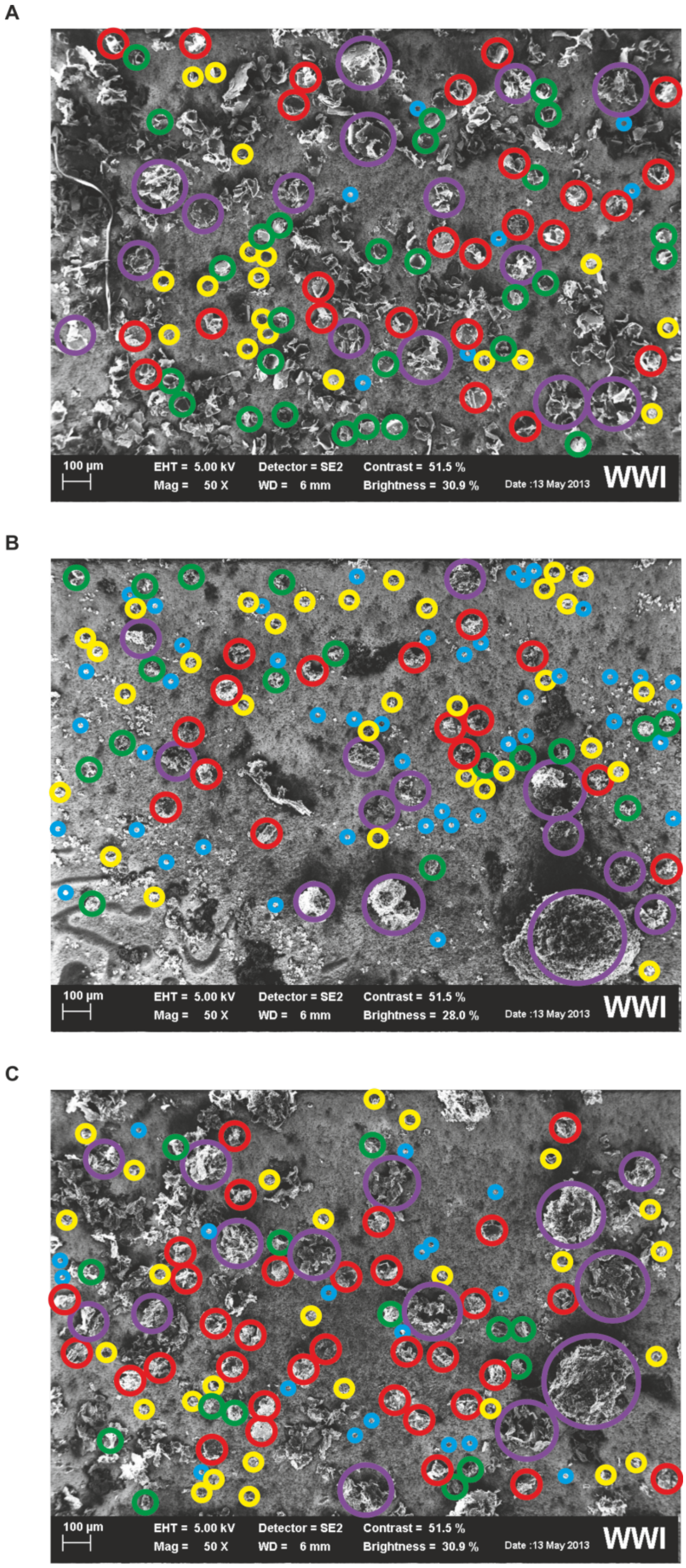


Figure S1: SEM images of A) $C_{12}H_{25}$-G(flake), B) $C_{12}H_{25}$-G(powder) and C) $C_{12}H_{25}$-G(spherical) for the determination of the grain size (see Table S4).

Acknowledgements: C. Krechel and the Chair of WW1 at the University of Erlangen-Nürnberg for providing the images.

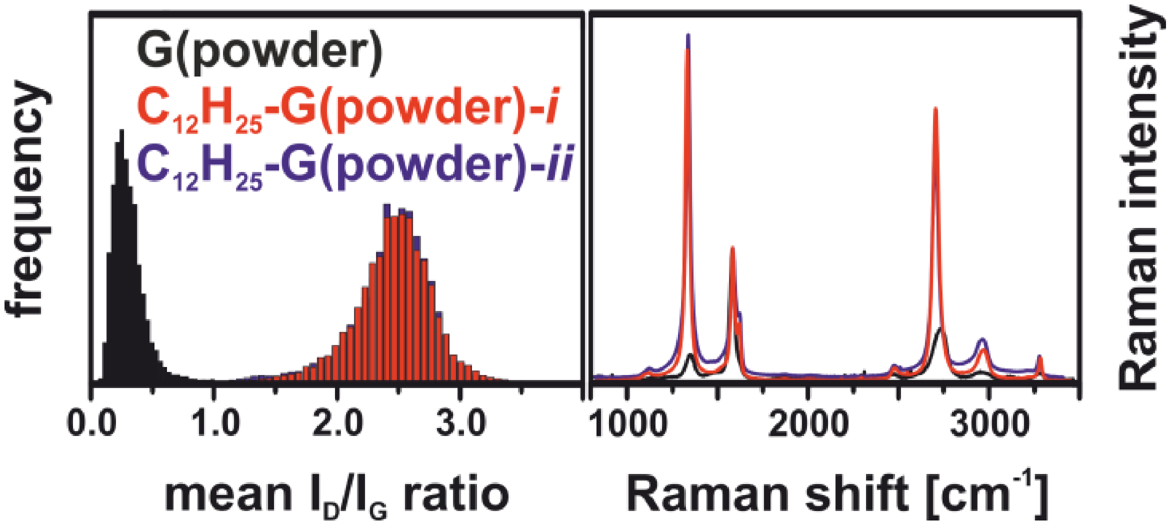


Figure S2: Left: Raman histograms (I_D/I_G-ratio) of the powder graphite (black) and two dodecyl-functionalized graphene samples (red and blue), prepared by the same procedure. Right: Correspondent averaged spectra (10,000 single point spectra) of the starting graphite and the functionalized materials, $\lambda_{exc.}$ = 532 nm.

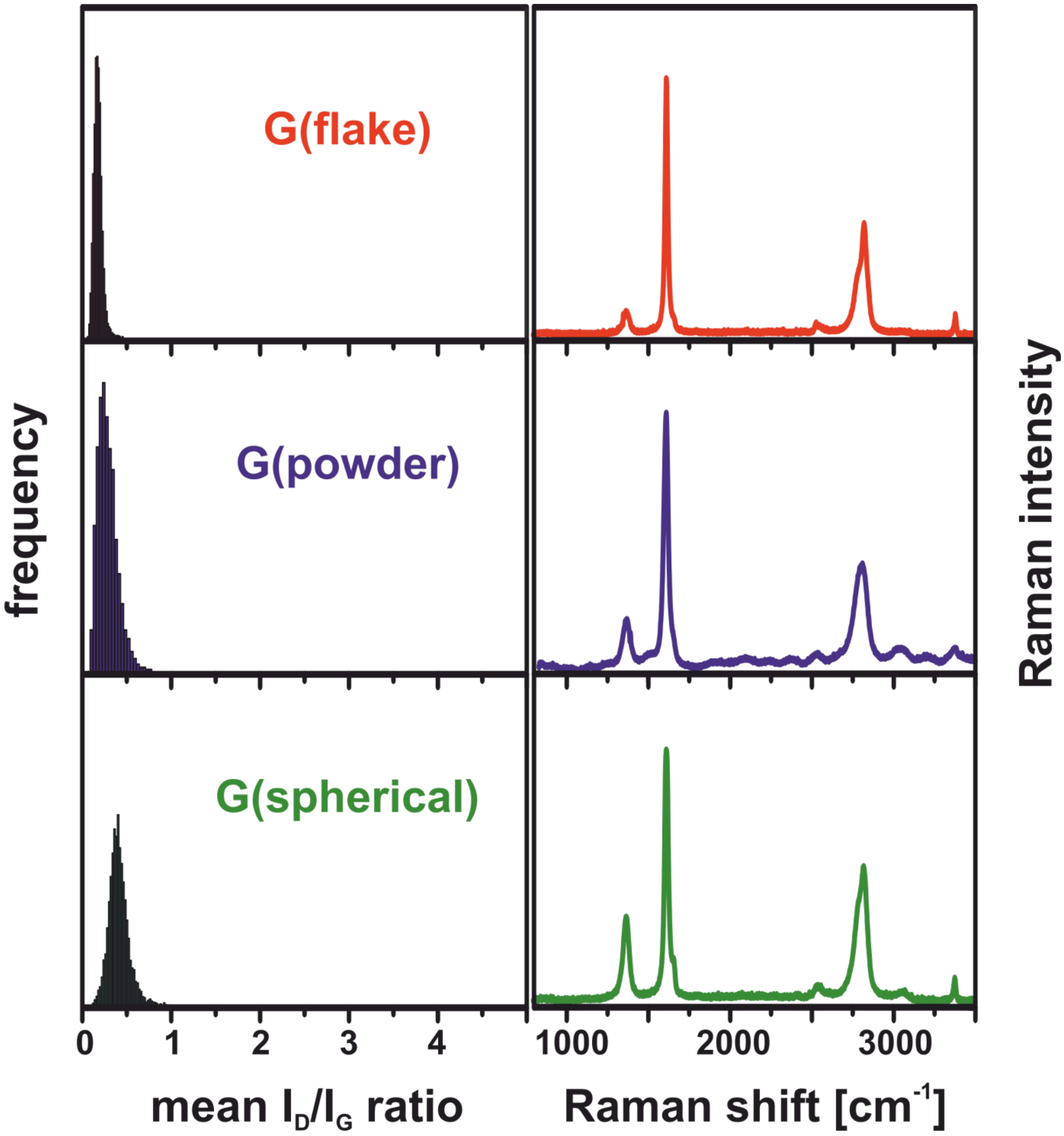


Figure S3: Raman histograms (I_D/I_G-ratio) and averaged Raman spectra (10,000 single point spectra) of the starting graphites, $\lambda_{exc.}$ = 532 nm - spectra normalized to G-band intensity.

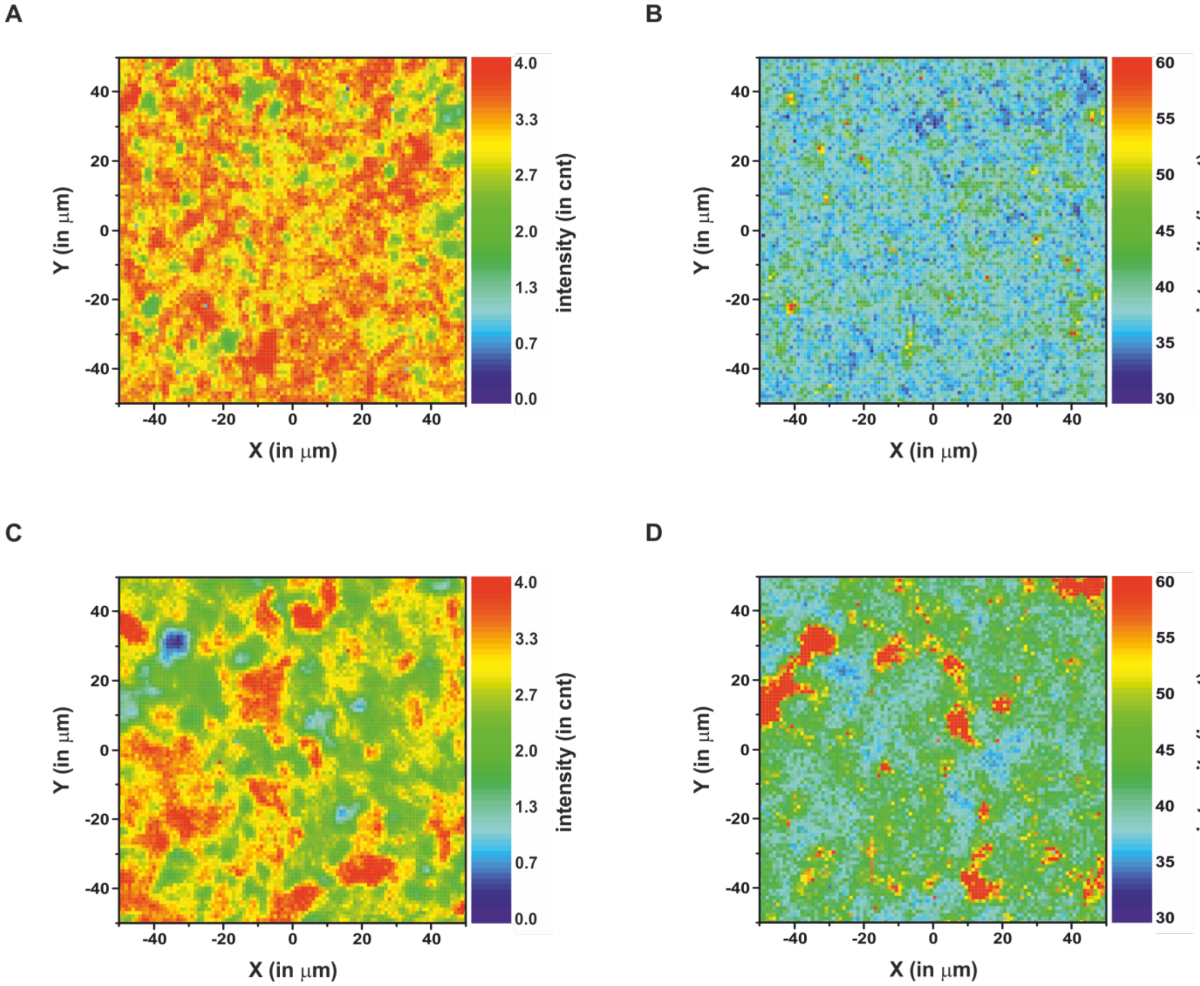


Figure S4: Raman maps of dodecyl-functionalized graphene samples: $\lambda_{exc.}$ = 532 nm, 10,000 μm^2; A) Mean I_D/I_G ratio of $C_{12}H_{25}$-G(powder) and B) FWHM of the respective 2D-band, C) Mean I_D/I_G ratio of $C_{12}H_{25}$-G(spherical) and D) FWHM of the respective 2D-band.

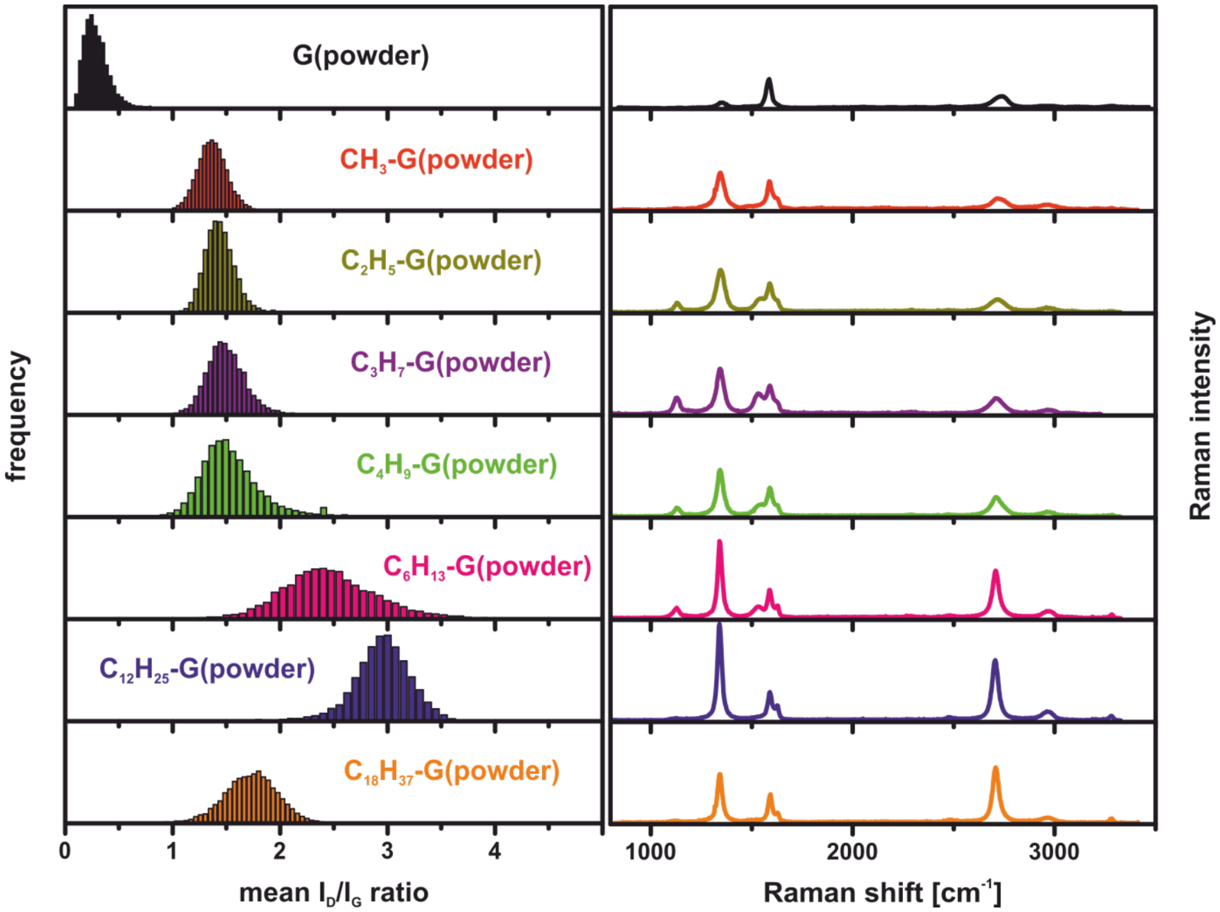


Figure S5: Raman histograms (I_D/I_G-ratio) and averaged Raman spectra (10,000 single point spectra) of the starting graphite (black) and the alkyl-functionalized materials (colour coded), $\lambda_{exc.}$ = 532 nm - spectra normalized to G-band intensity.

Table S5: Determined FWHM of the respective 2D-band of G(powder) and *n*-(C_nH_{2n+1})-G(powder) (n = 1-4, 6, 12, 18)

Type	Raman FWHM$_{2D}$ (in cm^{-1})
G(powder)	†
CH$_3$-G(powder)	†
C$_2$H$_5$-G(powder)	99
C$_3$H$_7$-G(powder)	90
C$_4$H$_9$-G(powder)	73
C$_6$H$_{13}$-G(powder)	39
C$_{12}$H$_{25}$-G(powder)	37
C$_{18}$H$_{37}$-G(powder)	37

†: a single Lorentz-fit is not suitable for this band

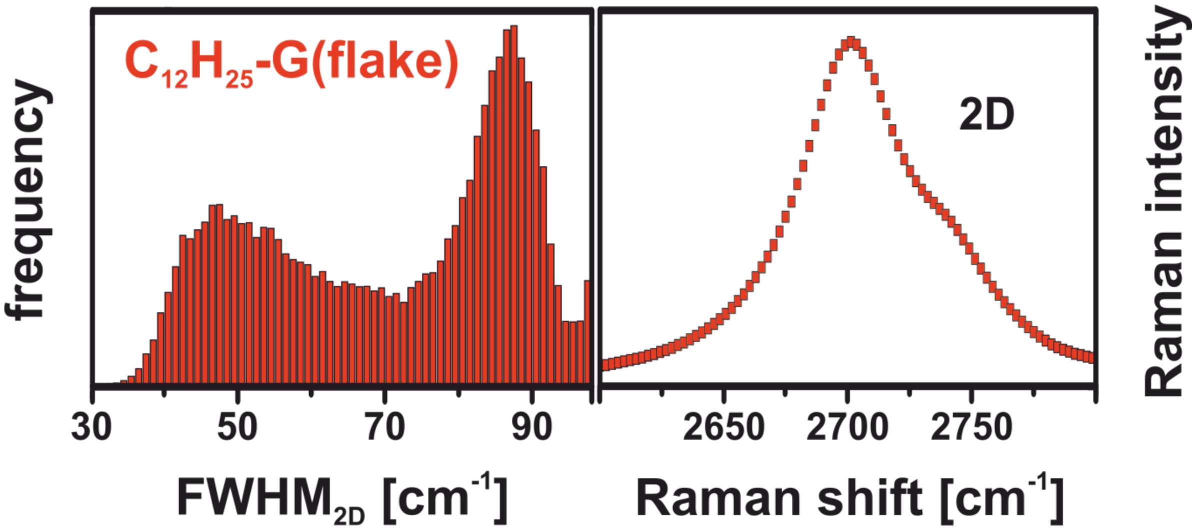


Figure S6: Left: Raman histogram (FWHM$_{2D}$) of the dodecyl-functionalized flake graphite. Right: Averaged spectrum (2D-band) of $C_{12}H_{25}$-G(flake), $\lambda_{exc.}$ = 532 nm.

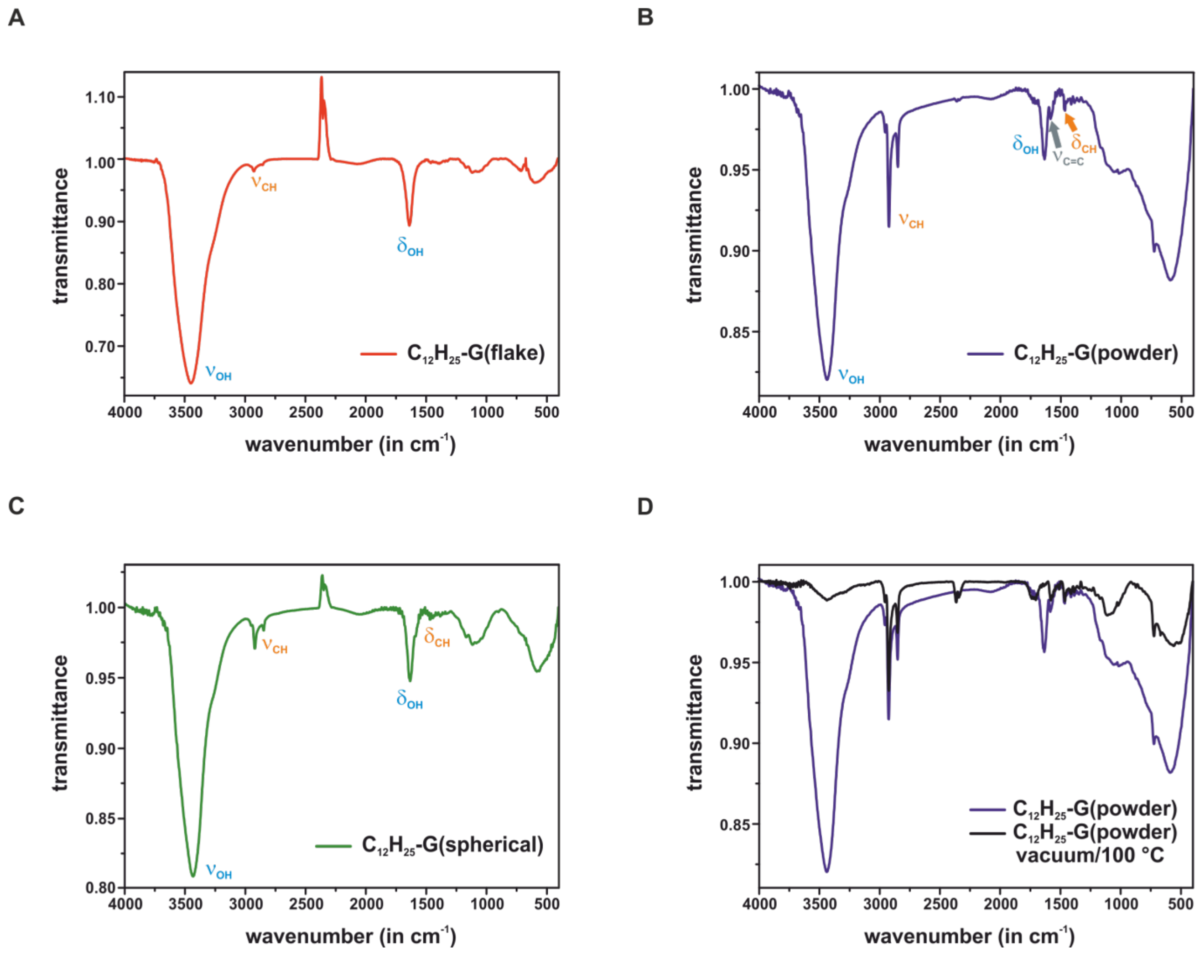


Figure S7: IR spectra of A) $C_{12}H_{25}$-G(flake), B) $C_{12}H_{25}$-G(powder), C) $C_{12}H_{25}$-G(spherical) and D) $C_{12}H_{25}$-G(powder) before and after heating the pellet at 100 °C in vacuum overnight.

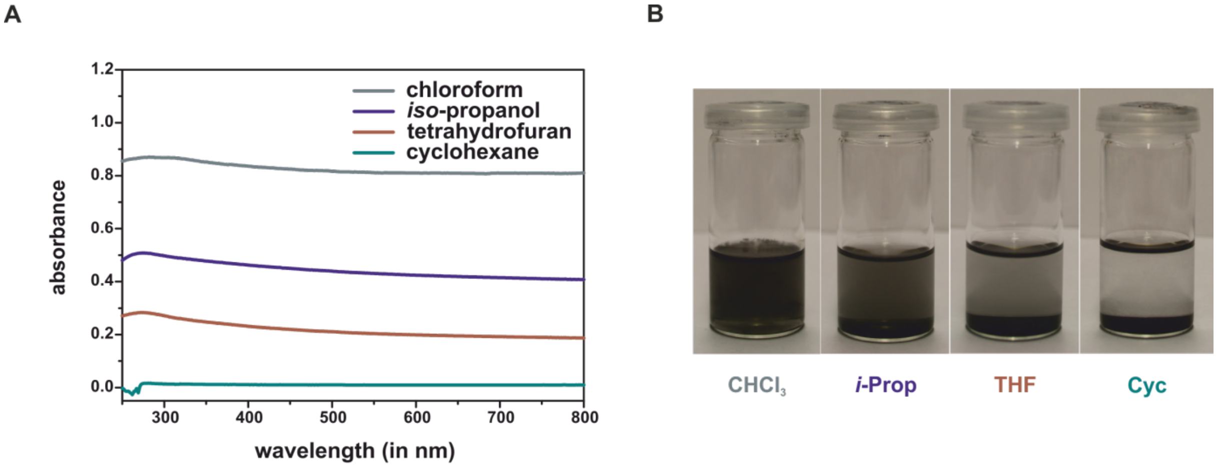
Potassium bromide pellets of the different samples were analysed via infrared spectroscopy.

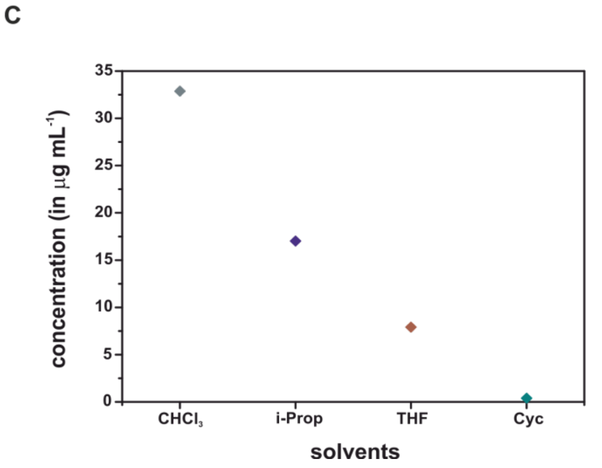
All the resulting infrared spectra show bands for adsorbed water. The bands (valence- and deformation vibration for OH) could be eliminated after vacuum treatment of the prepared pellets at 100 °C overnight. In addition a band for a CO-valence vibration at 1270 cm^{-1} is absent.

For the powder graphite a band for a CC-double bond valence vibration is characteristic.

Furthermore, bands for a CH-valence and -deformation vibration due to alkyl-chains arise, whereby the desired functionalization was able to be successfully proven.

In control-experiments, the arising of the alkyl bands due to side reactions, was able to be excluded and the starting materials also reveal no alkyl vibrations.





D

solvent	concentration (in µg mL^{-1})
chloroform	32.87
iso-propanol	17.01
tetrahydrofuran	7.90
cyclohexane	0.39

Figure S8: A) UV/vis spectra of dodecyl-functionalized powder graphite in different solvents (chloroform, *iso*-propanol, tetrahydrofuran, cyclohexane), B) correspondent dispersions and C), D) calculated concentrations.

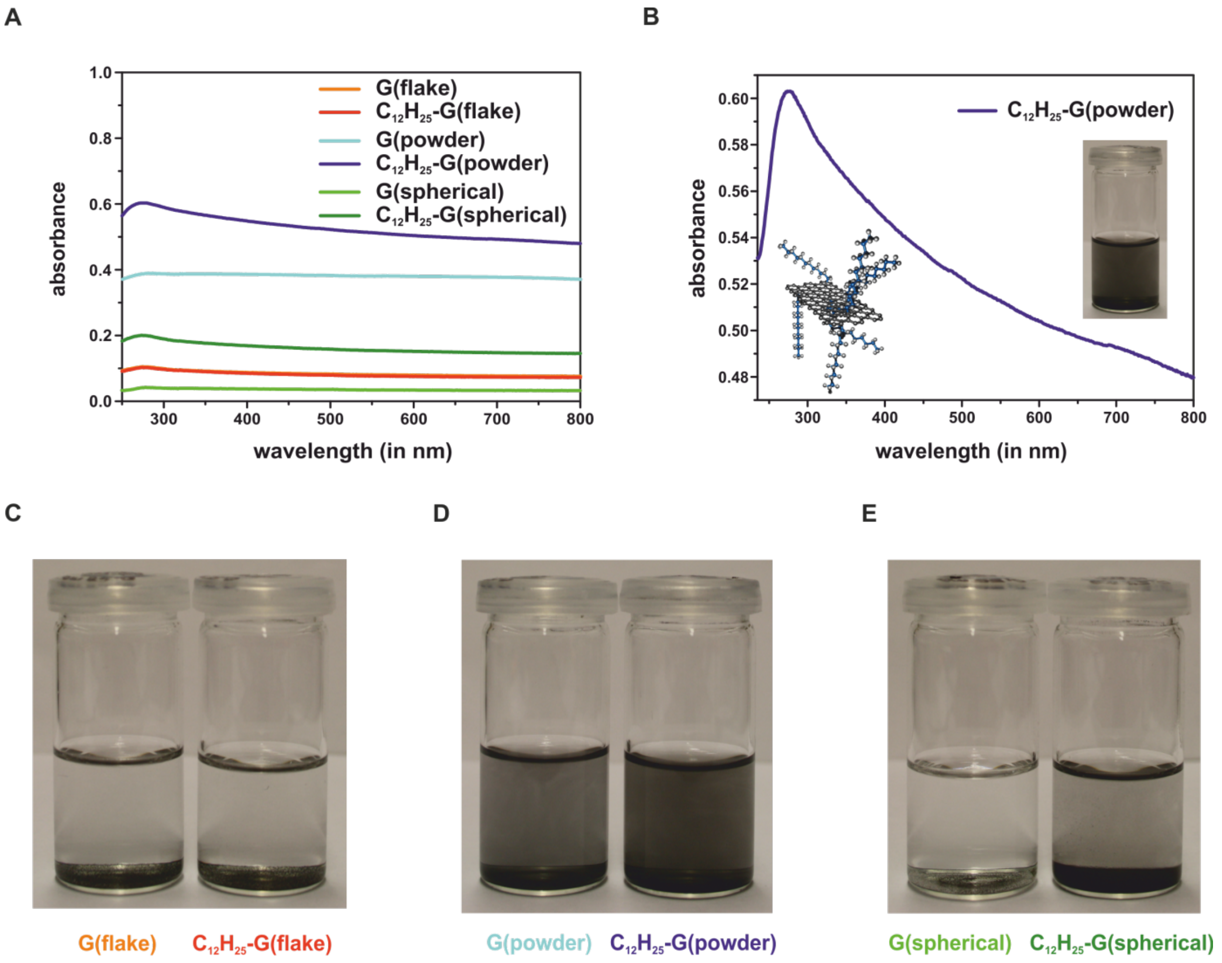
The samples were dispersed in the respective solvent (0.1 mg/mL) using an ultrasonic bath (*Bandelin*, *Sonorex Digital 10P*, *DK 255 P*, 640 W) for 10 minutes at 50 °C and left to sediment overnight.

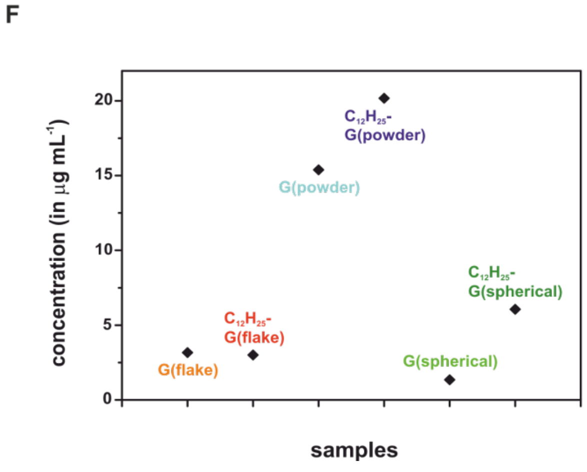
The UV/vis absorption spectra, measured from the respective supernatant, are featureless, except the single maximum observed from 273 nm (THF) to 282 nm ($CHCl_3$).

The photos were taken after the overnight sedimentation.

The dodecyl-functionalized powder graphite sample was chosen for the screening of an appropriate organic solvent, because this powdery material is the most dispersible.

This sample in particular exhibits an increased solubility in chloroform, as this study of absorption spectroscopy in common organic solvents reveals. However, to exclude particular dispersing effects in halogenated solvents, e.g. unwanted secondary functionalization, *iso*-propanol was chosen as a solvent for dispersion of alkylated material.





G

sample	concentration (in $\mu g\ mL^{-1}$)
G(flake)	3.16
$C_{12}H_{25}$-G(flake)	3.00
G(powder)	15.39
$C_{12}H_{25}$-G(powder)	20.17
G(spherical)	1.35
$C_{12}H_{25}$-G(spherical)	6.06

Figure S9: A) UV/vis spectra of pristine graphite and dodecyl-functionalized graphene, B) characteristic UV/vis spectrum of dodecyl-functionalized powder graphite and correspondent dispersions of pristine graphite (left) and dodecyl-functionalized graphene (right) in the case of C) flake graphite, D) powder graphite and E) spherical graphite and F), G) calculated concentrations.

The samples were dispersed in *iso*-propanol (initial concentration of 0.1 mg/mL) using an ultrasonic bath (*Bandelin*, *Sonorex Digital 10P*, *DK 255 P*, 640 W) for 10 minutes at 50 °C and left to sediment overnight. Then the supernatant, taken from the samples, was measured by UV/vis.

The photos were taken after the overnight sedimentation.