

Supporting Information for

The Ice Nucleation Activity of Graphene and Graphene Oxides

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XPS-revealed carbon components

Table S1 XPS-determined carbon components of all investigated samples.

	Component at% of C1s signal						
	Csp2	C-C/C-H	C-O	C=O	O-C=O	C shake up	C shake up2
Graphene							
G-non	85.5	7.5	3.1	0.5		2.8	0.5
G-NPr ₃ ⁺ I ⁻	90.7	1.9	3.1		0.7	3.3	0.3
G-NPr ₃ ⁺ OH ⁻	72.2	19.1	5.3	3.4			
Graphene oxides							
GO-DE	45.1	18.4	25.0	1.8	2.9	3.3	3.6
GO-SA	29.2	21.2	33.3	2.7	2.8	7.2	3.5
GO-NH ₂	42.0	22.5	20.9	3.1	2.5	6.1	3.0
GO-nano	18.5	12.5	37.5	13.7	11.6	6.3	

Graphene and graphene oxide suspensions

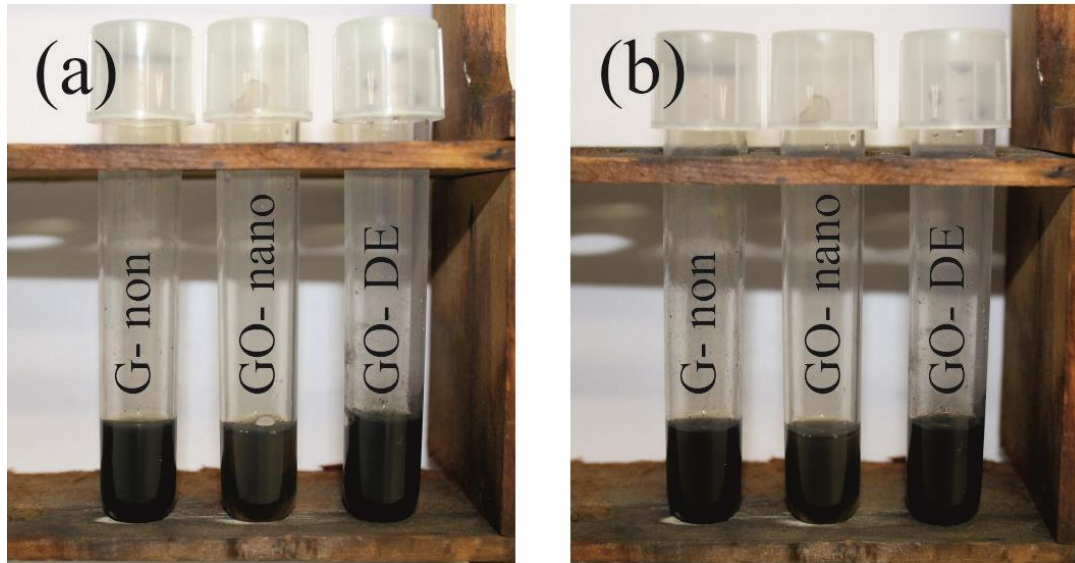


Figure S1 Graphene and graphene oxide suspensions with concentrations of 0.8 % for G-non and GO-DE, 0.2 % for GO-nano (a) immediately after sonication for 5 minutes and (b) after settling for 30 minutes.

Refreezing experiment of G-non

A refreezing experiment with G-non was performed to demonstrate that no migration into the oil phase takes place during the experiment. Any migration of INP into the oil phase during the freezing process would lead to a decrease of surface area and hence INA. As demonstrated in Figure S2, no decrease of INA can be observed. We assume that due to the high viscosity of supercooled water at operating temperatures below 0 °C no migration into the oil phase takes place.

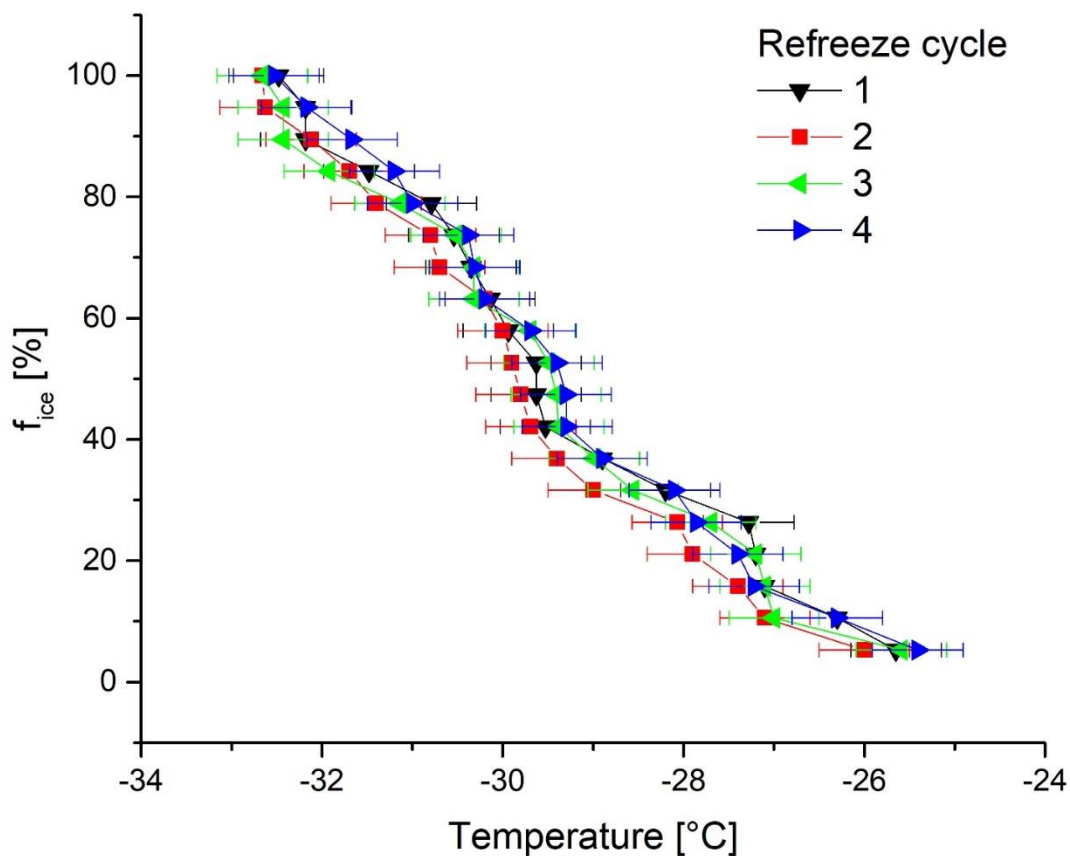
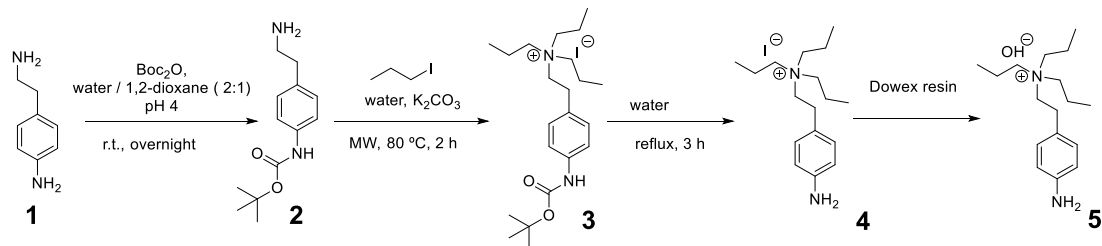


Figure S2 Freezing spectra of refreezing experiment with G-non. Error bars are accordingly to a temperature uncertainty of ± 0.5 °C.

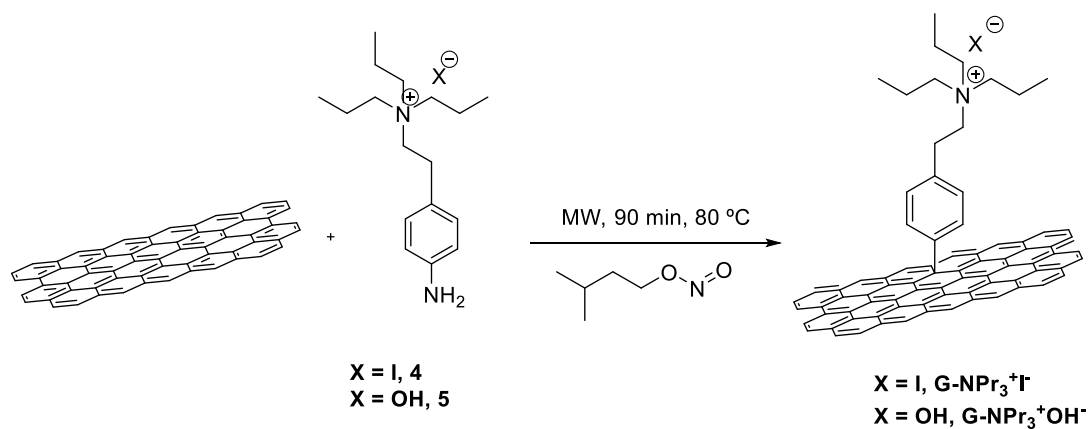
Synthesis and characterization of functionalized graphene samples (G-NPr₃⁺X⁻)

Thermogravimetric analyses (TGA) of approximately 1 mg of each compound were recorded on a TGA Q500 (TA Instruments) under N₂, by equilibrating at 100 °C, and following a ramp of 10 °C min⁻¹ up to 800 °C. Raman spectra were recorded with an Invia Renishaw microspectrometer (50) equipped with He–Ne laser at 532 nm. Powders were dispersed in EtOH, drop-casted onto silicon wafer and the solvent evaporated; at least 20 spectra per sample were recorded on different areas of the sample in order to check the uniformity of the materials. Transmission Electron Microscopy (TEM) measurements were performed on a TEM Philips EM208, using an acceleration voltage of 100 kV. Samples were prepared by drop casting from the dispersion onto a TEM grid (200 mesh, copper, carbon only).

Synthesis of functionalized graphene:

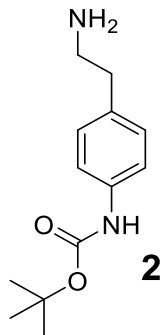


Scheme S1. Synthesis of the grafting agent.



Scheme S2. Functionalization of G.

4-(2-aminoethyl)-N-(tert-butoxycarbonyl)phenylamine (2).



A reported protocol was followed for the synthesis of **2**.¹ Briefly, in a round-bottom flask, 4-(2-aminoethyl)-N-(*tert*-butoxycarbonyl)phenylamine (1 g, 734 μmol) was dissolved in acetic acid (aq) 10 % (60 ml). To this solution, Boc₂O (1.64 g, 7.5 μmol) in 1,4-dioxane (60 ml) were

slowly added. After stirring for 16 h at r.t., the crude was diluted with deionised water (150 ml) and then washed with Et₂O (3 x 75 ml). The aqueous phase was basified with NaOH 2M to pH 14 and extracted with Et₂O (3 x 100 ml). The combined organic phases were washed with deionized H₂O (2 x 50 ml), dried with Na₂SO₄ and filtered. The solvent was eliminated under reduced pressure affording product **2** (1.14 g 66 %). **¹H NMR** (500 MHz, CD₃OD) δ 7.26 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.05 (d, *J* = 8.3 Hz, 2 H, Ar-H), 2.78 (t, *J* = 7.2 Hz, 2H, Ar-CH₂), 2.63 (t, *J* = 7.2 Hz, 2 H, -CH₂-N), 1.45 (s, 9 H, 3 x -CH₃). **¹³C NMR** (125 MHz, CD₃OD): δ 155.6, 138.9, 135.3, 130.2, 120.3, 80.9, 44.3, 39.5, 28.9 **MS (ESI)**: *m/z* 234.8 [M]⁺, 179.6 [M-56.5]; 163.1 [M-90]. C₁₃H₂₀N₂O₂ requires 236.1.

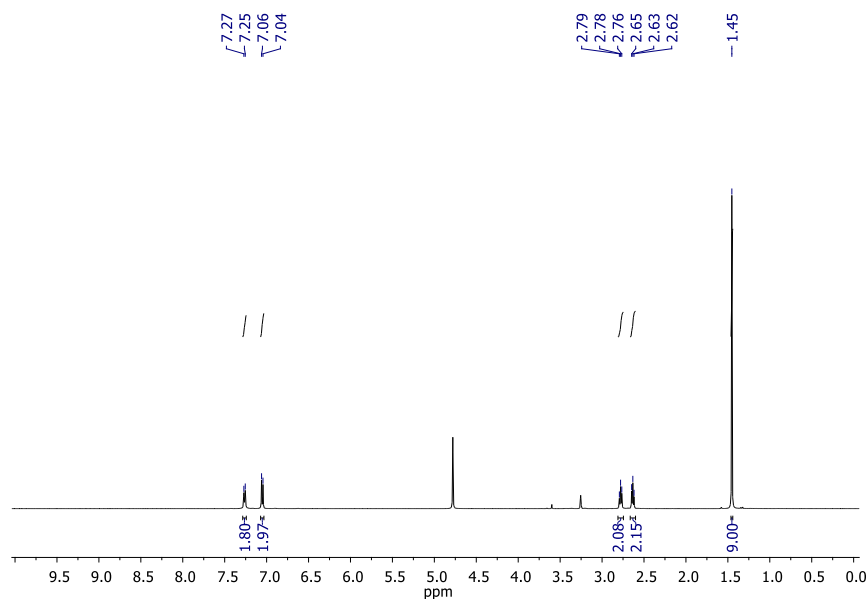


Figure S3. ¹H-NMR spectrum of **2** in CD₃OD.

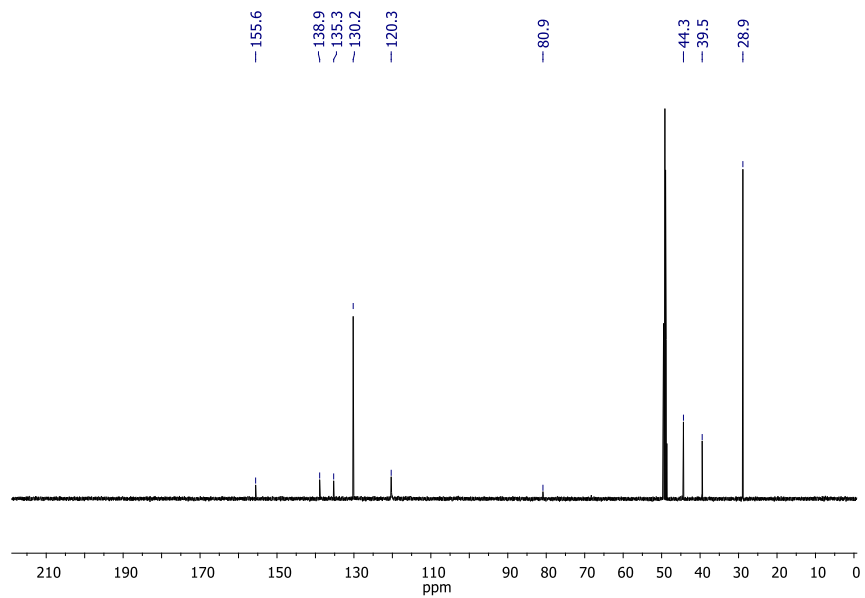


Figure S4. ^{13}C -NMR of product 2 in CD_3OD .

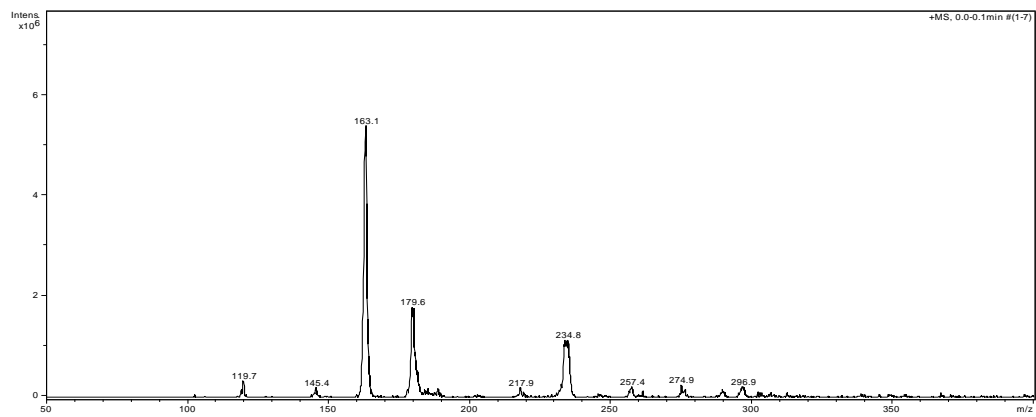
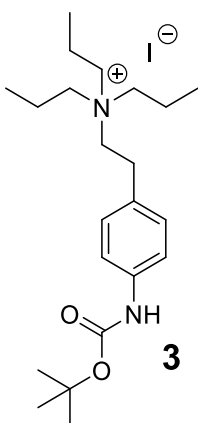


Figure S5. Mass spectrum of 1.

1-(triisopropylammonioethyl)-4-(N-tertbutoxycarbonyl)phenylamine iodide (**3**)



The synthesis of **3** was adapted from literature.² Briefly, **2** (0.75 g, 3.2 mmol), propyl iodide (6 ml, 60.00 mmol), potassium carbonate (2.25 g, 16.28 mmol) and deionized H₂O (11 ml) were poured in a round bottom flask creating a biphasic system. A condenser was connected and the reaction was irradiated for 2 h at 80 °C setting the maximum irradiation power at 100 W. After the irradiation, the crude appeared to be a triphasic system being the desired product in between the aqueous and the organic phase. The water phase was eliminated from the top with a pipette. Then, hexane (20 ml) were added and the crude was filtered. Hexane (3 x 20 ml) were used to clean the product and the crude was dried under vacuum obtaining **3** as a yellow solid (64 %). ¹H NMR (500 MHz, CD₃OD) δ (ppm): 7.33 (d, *J* = 7.2 Hz, 2 H, Ar.), 7.16 (d, *J* = 7.2 Hz, 2 H, Ar.), 3.38 (m, 2 H, CH₂-N), 3.23 (m, 6 H, 3 x CH₂-N), 2.92 (m, 2 H, *o*-CH₂), 1.97 (m, 6 H, 3 x CH₂), 1.45 (s, 9H, 3 x CH₃), 0.96 (t, *J* = 1.0 Hz, 9 H, 3 x CH₃). MS (ESI): *m/z* 363.2 [M⁺] C₂₂H₃₉N₂O₂⁺ requires 362.2

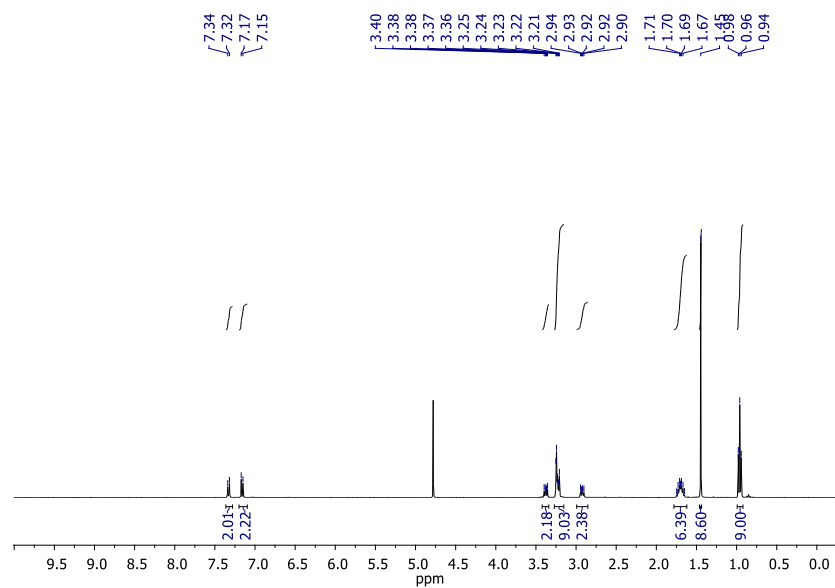


Figure S6. ^1H -NMR spectra of 3 in CD_3OD .

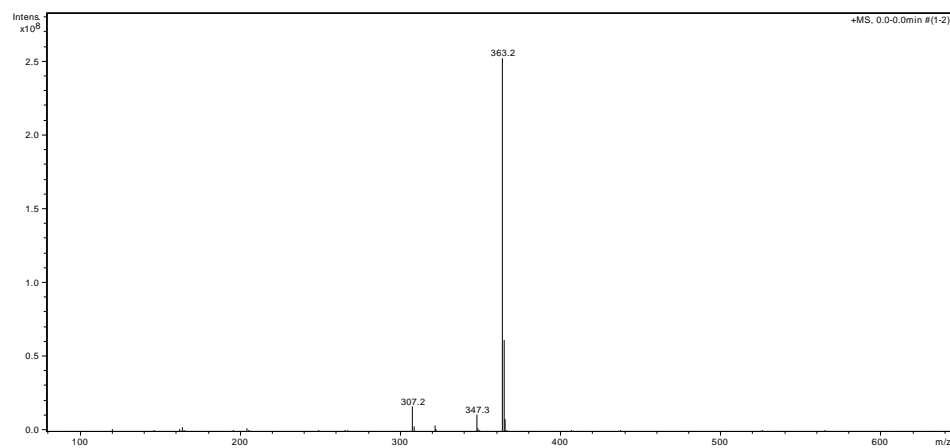
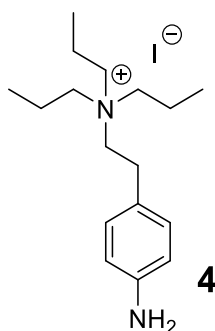


Figure S7. Mass spectrum of 3.

4-aminophenethyltripropyl ammonium iodide (**4**).



The synthesis of **4** was adapted from literature.³ **3** (520 mg, 1.0 mmol) was refluxed in deionized water (50 ml) for 3 h. The crude of reaction was freeze-dried obtaining **4** as a yellowish solid (85 %). **¹H NMR** (500 MHz, CD₃OD): δ 7.10 (d, *J* = 10 Hz, 2 H, Ar-H), 6.76 (d, *J* = 10 Hz, 2H, Ar-H), 3.44 (t, *J* = 10 Hz, Ar-CH₂), 3.33 (m, 6H, -CH₂-N), 2.95 (t, *J* = 9 Hz, 2H, -CH₂-N), 1.80 (m, 6H, -CH₂-), 1.06 (t, *J* = 8 Hz, 3H, CH₃-). **¹³C NMR** (125 MHz, CD₃OD) δ 148.3, 130.8, 126.1, 117.1, 61.5, 61.2, 28.8, 16.7, 11.1. **MS (ESI+)** *m/z* calcd for C₁₆H₁₄N₂O₂⁺ 263.2, found *m/z* 263.6 [M]⁺, **MS (ESI-)** *m/z* calcd for I⁻ 126.9, found *m/z* 126.8 [I⁻].

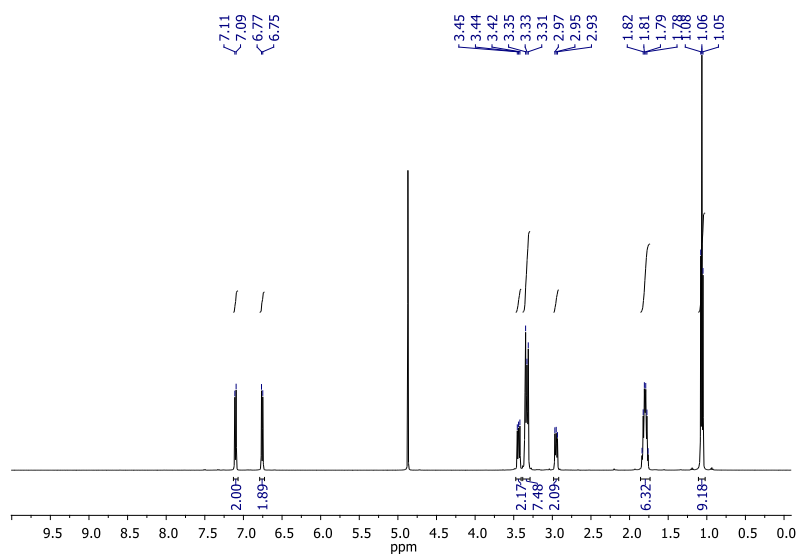


Figure S8. ¹H-NMR spectra of **4** in CD₃OD.

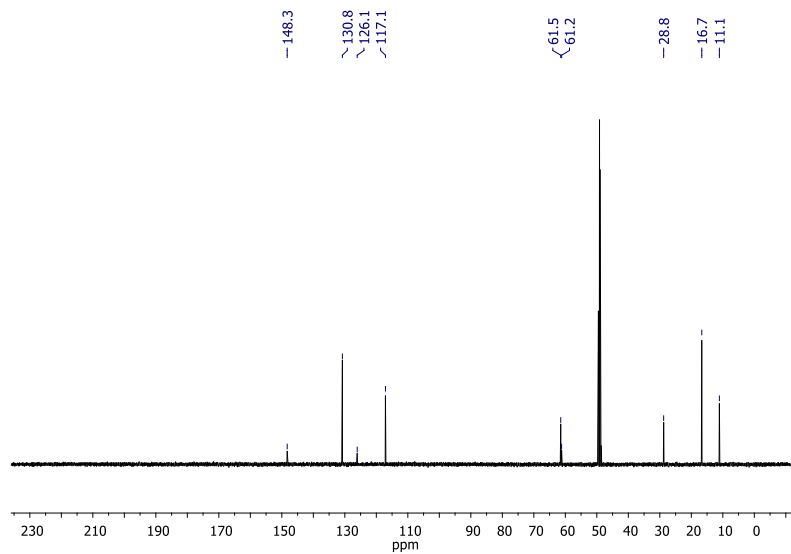


Figure S9. ^{13}C -NMR spectra of 4 in CD_3OD .

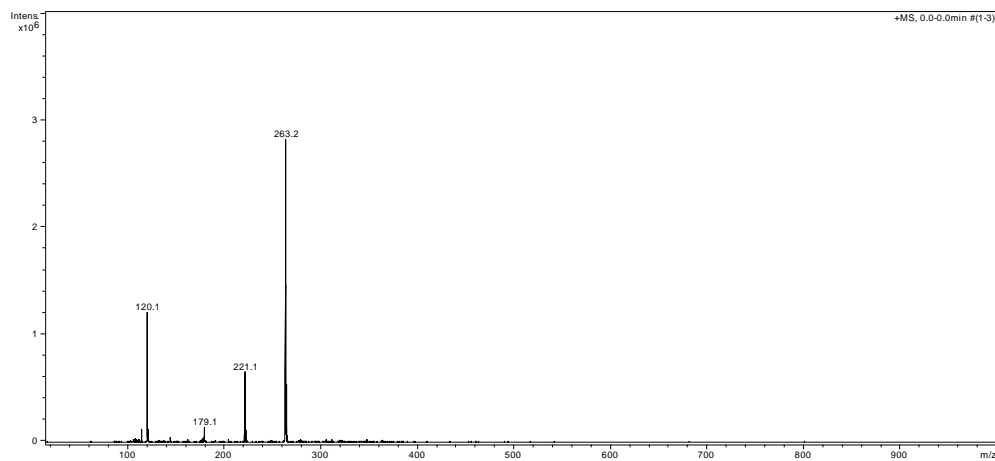


Figure S10. Mass spectrum of 4.

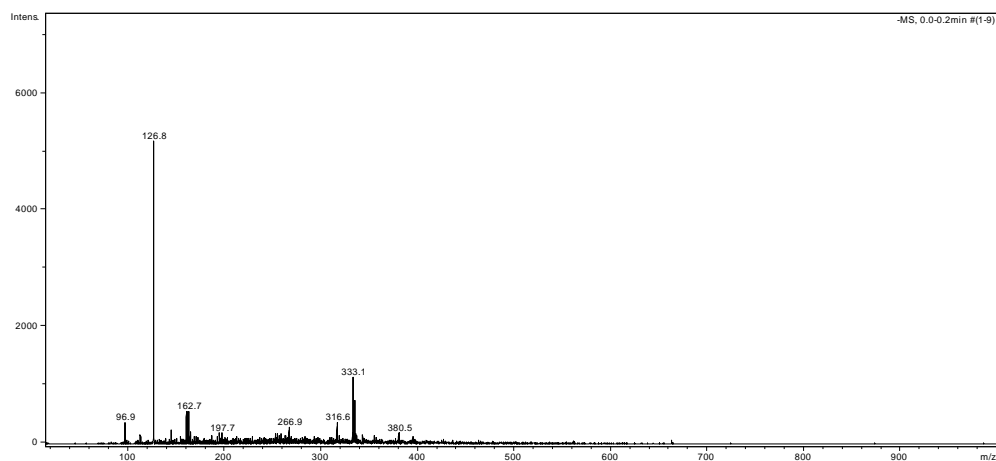
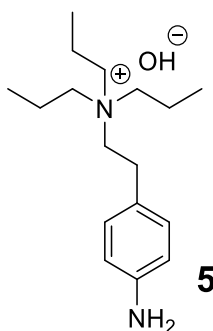


Figure S11. Mass spectrum of **4** (negative mode showing the presence of I⁻).

4-aminophenethyltripropyl ammonium hydroxide (5**).**



For the anion exchange process, KOH 1 M (5 ml) were passed through 2 ml of Dowex® resin (chloride form, 100-200 mesh). Next, the resin was washed with deionized water until its neutralization. Then, a solution of product **4** (0.07 M) in H₂O was passed slowly through the resin and the resin was eventually washed with H₂O/MeOH 4/1 (20 ml). Finally, the solvent was eliminated under reduced pressure affording product **5** as a yellowish product. ¹H NMR confirmed the identity of product **5**. MS (ESI⁺) *m/z* calcd for C₁₆H₁₄N₂O₂⁺ 263.2, found *m/z* 263.6 [M]⁺, MS (ESI⁻) absence of I⁻.

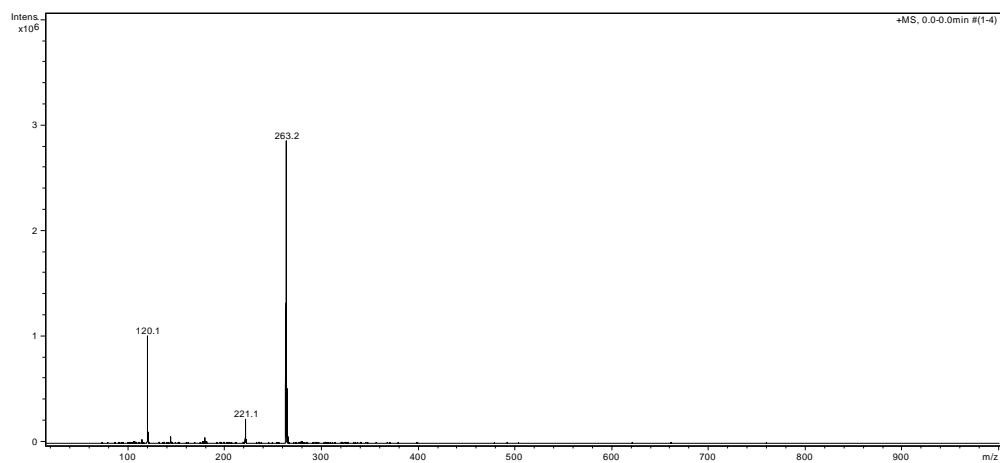


Figure S12. Mass spectrum of 5.

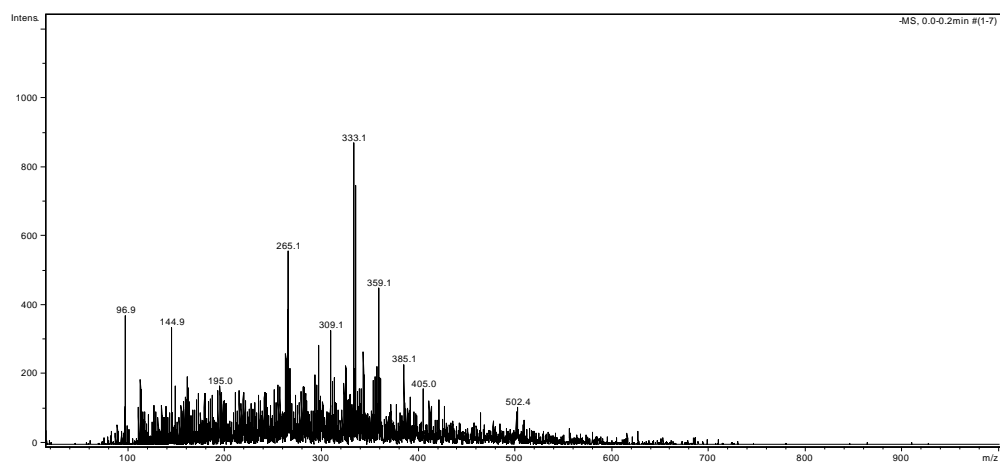


Figure S13. Mass spectrum of 5 (negative mode showing the absence of I⁻).

G-NPr₃⁺X⁻

Graphene dispersion in water was supplied by Thomas Swan Co., Ltd.

A protocol reported for the functionalization of carbon nanotubes was adapted for the functionalization of graphene.⁴ In a typical experiment, 45 ml of graphene dispersion (0.84 g l⁻¹) and **4** or **5** (0.96 mmol) were sonicated for 5 min. Then, isopentyl nitrite (0.35 ml, 2.5 mmol) was added and the mixture was irradiated with microwaves at 80 °C setting the maximum irradiation power at 100 W. After 30 min irradiation a second aliquot of isopentyl nitrite (0.35 ml, 2.5 mmol) was added and the reaction was irradiated at 80 °C for 1 h setting the maximum power at 30 W. Once the reaction cooled down, the crude was filtered through a Millipore membrane (JHWP, 0.45 μm). The black powder was purified through several cycles of sonication/filtration with DMF, deionized water, EtOH and MeOH till the washings were clean. Eventually, the black powder was washed with Et₂O and dried under vacuum.

Control-graphene.

In a round-bottom flask, 17 ml of graphene dispersion (0.84 g l⁻¹) were sonicated for 5 min. Then, the mixture was irradiated with microwaves at 80 °C setting the maximum irradiation power at 100 W. After 30 min irradiation a second irradiation step was done at 80 °C for 1 h setting the maximum power at 30 W. Once the reaction cooled down, the crude was filtered through a Millipore membrane (JHWP, 0.45 μm). The black powder was purified through several cycles of sonication/filtration with DMF, deionized water, EtOH and MeOH till the washings were clean. Eventually, the black powder was washed with Et₂O and dried under vacuum affording 13 mg of **control-G**.

Characterization of functionalized graphene

Thermogravimetric analysis (TGA) in N₂

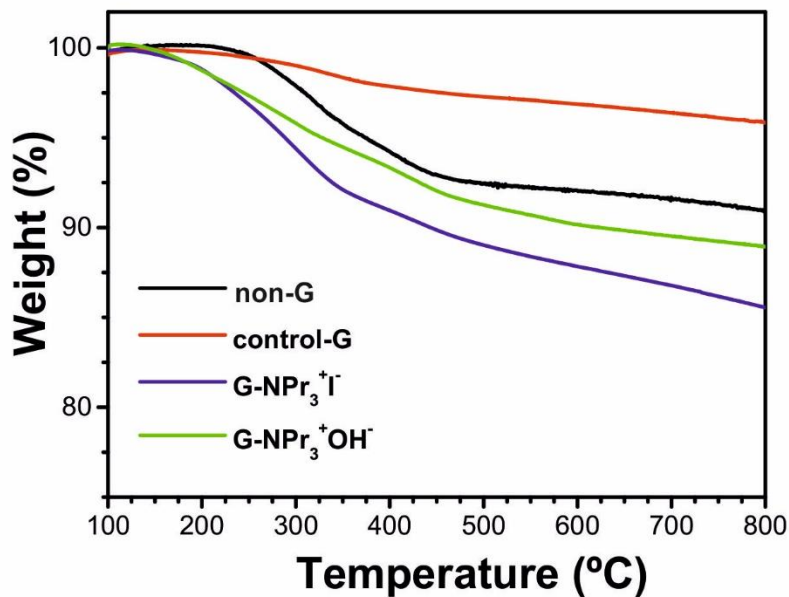


Figure S14. Thermogravimetric analysis (N₂) of the different graphene samples.

TGA allows the calculation of the degree of functionalisation. In this case, the degree of functionalisation is 0.34 mmol of FG/g for **G-NPr₃⁺I⁻** and 0.28 mmol FG/g of **G-NPr₃⁺OH⁻**. The degree of functionalisation was calculated by comparison of the weight loss of **blank-G** and the functionalized samples at 600 °C.

Raman analysis (532 nm)

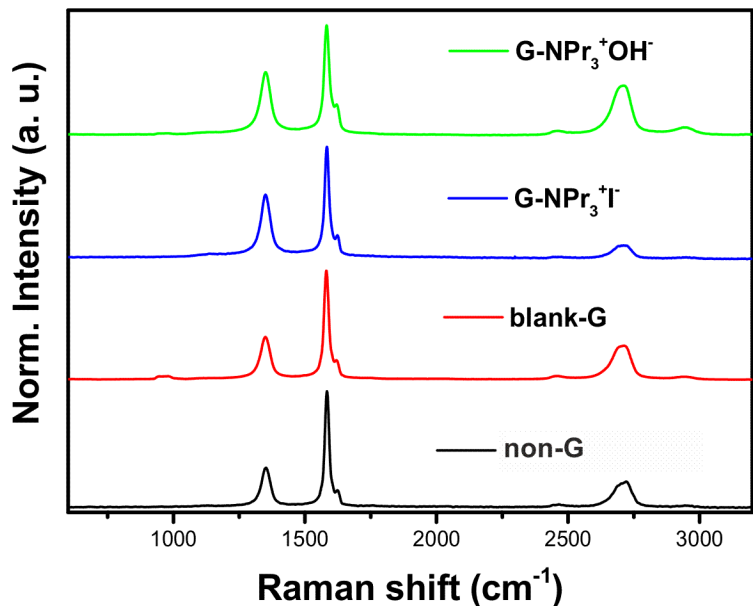


Figure S15. Raman analysis (532 nm) of the different graphene samples.

I_D/I_G ratio were 0.33 ± 0.05 ; 0.39 ± 0.06 ; 0.58 ± 0.05 ; and 0.57 ± 0.05 for **non-G**, **blank-G**, **G-NPr₃⁺I⁻**, **G-NPr₃⁺OH⁻** confirming the functionalization. I_D/I_G ratio increase due the presence of more sp^3 C atoms after the covalent functionalization. Besides, Raman analysis confirmed that microwaves do not alter the carbon lattice of graphene.

TEM images

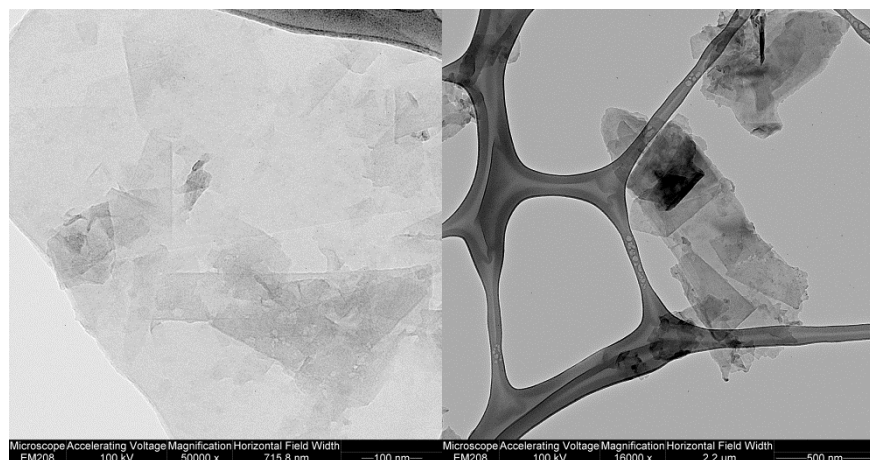


Figure S16. TEM images of G-NPr₃⁺OH⁻.

TEM reveals that the protocol preserves the structure of the graphene flakes.

References

1. Perron, V.; Abbott, S.; Moreau, N.; Lee, D.; Penney, C.; Zacharie, B., A Method for the Selective Protection of Aromatic Amines in the Presence of Aliphatic Amines. *Synthesis-Stuttgart* **2009**, 283-289.
2. Ju, Y. H.; Varma, R. S., An Efficient and Simple Aqueous N-Heterocyclization of Aniline Derivatives: Microwave-Assisted Synthesis of N-Aryl Azacycloalkanes. *Org. Lett.* **2005**, 7, 2409-2411.
3. Medina-Ramos, W.; Mojica, M. A.; Cope, E. D.; Hart, R. J.; Pollet, P.; Eckert, C. A.; Liotta, C. L., Water at Elevated Temperatures (Wet): Reactant, Catalyst, and Solvent in the Selective Hydrolysis of Protecting Groups. *Green Chem.* **2014**, 16, 2147-2155.
4. Brunetti, F. G.; Herrero, M. A.; Munoz, J. D.; Diaz-Ortiz, A.; Alfonsi, J.; Meneghetti, M.; Prato, M.; Vazquez, E., Microwave-Induced Multiple Functionalization of Carbon Nanotubes. *J. Am. Chem. Soc.* **2008**, 130, 8094-8100.