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Supporting Information

Covalent functionalization of N-doped graphene by N-alkylation†

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Material and Instrumentation

All chemicals were obtained from commercial sources and used as received. N- graphene was obtained by pyrolysis of chitosan beads at 900 ºC under inert atmosphere.[1] Sample sonication was carried out using an Elmasonic P 300 h sonicator bath (37 kHz). Reactions were performed under phase transfer catalysis (PTC) conditions and by classical heating and microwave irradiation in a CEM Discover reactor, with fiber optic temperature and pressure control. Steady-state absorption spectra in the visible region were measured on a Shimatzu UV 3600 spectrophotometer. IR spectra were obtained on a Fourier Transform IR spectrophotometer (Avatar 370) in KBr pellets. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. Raman spectra were performed on Renishaw inVia Raman instrument coupled with a Leica microscope at room temperature with a 532 nm exciting laser. AFM images were acquired in tapping mode using a Multimode V8.10 (Veeco Instruments Inc., Santa Barbara, USA) with a NanoScope V controller (Digital Instruments, Santa Barbara, USA). The cantilevers (RTESP from Bruke Probes) were silicon cantilevers with a resonance frequency of 300 kHz and a nominal force constant of 40 Nm^{-1}.The functionalized samples (1 mg mL^{-1}) were prepared by sonication (frequency: 37 kHz; power 380 W) in milli-Q water for 90 min. Samples were prepared by dropcast method on SiO_2 surfaces. TEM imaging was performed on a JEOL 2100 microscope at 200 kV. The N-graphene samples were dispersed in acetone and sonicated for 15 min. The resulting suspension was dropped onto a holey carbon copper grid, and the solvent was allowed to evaporate. Thermogravimetric analyses were performed under nitrogen atmosphere using a Mettler-Toledo model TGA/SDTA851e with a heating rate of 10 ºC/min. Photoelectron spectra (XPS) were recorded with a VG Escalab 200R spectrometer provided with a hemispherical electron analyser and MgKα (hν = 1253.6 eV) X-ray source, powered at 100 W. The background pressure in the analysis chamber was kept below 8×10^{-9} mbar during data acquisition. The high resolution XPS spectra were recorded at constant pass energy of 50 eV, in increments of 0.1 eV with dwell times of 40 ms. Charge effects on the samples were corrected by taking the binding energy (BE) of C 1s peak at 284.8 eV. High resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software "XPS peak". The raw data were used with no preliminary smoothing. Symmetric Gaussian-Lorentzian (90%G-10%L) lines were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors. The peaks in the core-level spectra were fit using commercial "*XPS peak"* analysis software. The raw data were used with no preliminary smoothing. Symmetric Gaussian-Lorentzian (90%G-10%L) lines were used to approximate the line shapes of the fitting components. In most cases, the full widths at half maximum (FWHM's) converged to consistent values throughout the series without being restricted but for a few peaks they were fixed based on values for corresponding spectra with the highest signal-to-noise ratio in the series. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors.

The optical bandgap of (N)G and *functionalized* NG samples **1-4** was determined from the linear extrapolation of the Tauc plot of the modified Kubelka-Munk function of the reflectivity in the UV-Vis spectra of aqueous suspensions of these materials.

N Graphene exfoliation procedure

Exfoliation was performed by sonication using an Elmasonic P 300 H sonicator bath (37 kHz). After 30 min of sonication the resulting dispersion was centrifuged for 10 min at 500 rpm and the supernatant was separated from the bottom product by pipetting the liquid phase. The concentration in the resulting dispersions was determined by recording the absorbance at 660 nm and transforming this into the concentration using the Lambert-Beer law $A/l=\alpha c$ with a α=2.460 L/mg/m.[2]

Synthetic procedure

General procedure for the reaction under classical heating (CH)

To a suspension of N-graphene (3 mg) in water (100 mL), potassium carbonate (K_2CO_3) (2 equiv), tetra-n-butylammonium bromide (TBAB) (4 equiv) and the corresponding bromide derivative dissolved in 5 mL of dichloromethane (CH_2Cl_2) were added. The reaction was stirred for 20 h at 70 ºC. The solvent was evaporated under reduced pressure and the crude product was then washed several times with methanol and CH_2Cl_2.

Synthesis of *f*-NG 1.According to the general procedure, the following compounds and materials N-graphene (3 mg), K_2CO_3 (69.1 mg, 0.5 mmol), TBAB (322.5 mg, 1 mmol) and 2-bromo-4′-chloroacetophenone (584 mg, 2.5 mmol) were reacted affording 13 mg of ***f*-NG 1**.

Synthesis of *f*-NG 2. According to the general procedure, N-graphene (3 mg), K_2CO_3 (69.1 mg, 0.5 mmol), TBAB (322.5 mg, 1 mmol) and 3-phenoxypropyl bromide (538 mg, 2.5 mmol) were reacted to afford 9 mg of ***f*-NG 2**.

Synthesis of *f*-NG 3. According to the general procedure, N-graphene (3 mg), K_2CO_3 (69.1 mg, 0.5 mmol), TBAB (322.5 mg, 1 mmol) and 4-(trifluoromethyl)-benzyl bromide (598 mg, 2.5 mmol) were reacted to afford 10 mg.

General procedure for the reaction under microwave irradiation (MW)

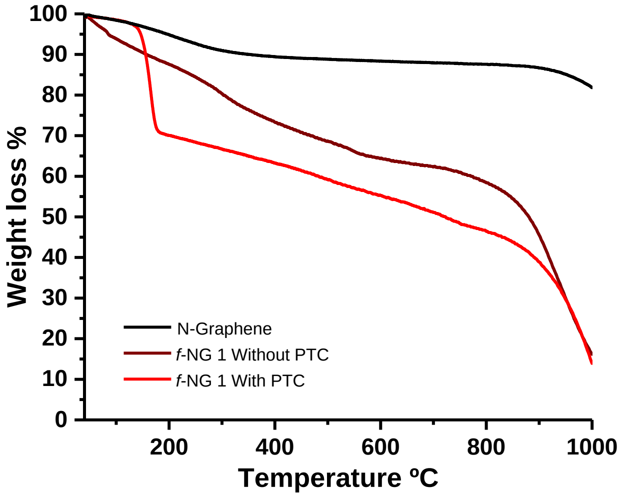
To a suspension of N-graphene (4.7 mg) in water (80 mL), K_2CO_3 (2 equiv), TBAB (4 equiv) and corresponding the bromide derivative dissolved in 5 mL of CH_2Cl_2 were added. Single-mode microwave irradiation (5W) was applied for 60 min at 70 ºC. The reaction was then allowed to reach room temperature, and the crude product was separated by centrifugation, decanted, and then washed several times with methanol and CH_2Cl_2.

Synthesis of *f*-NG 1. According to the general procedure N-graphene (4.7 mg), $K_2CO_3K_2$ (110 mg, 0.8 mmol), TBAB (516 mg, 1.6 mmol) and 2-bromo-4′-chloroacetophenone (918 mg, 3.93 mmol) afforded 13 mg.

Synthesis of *f*-NG 2. According to the general procedure, N-graphene (4.7 mg), K_2CO_3 (110 mg, 0.8 mmol), TBAB (516 mg, 1.6 mmol) and 3-phenoxypropyl bromide (0.62 mL, 3.94 mmol) afforded 10 mg.

Synthesis of *f*-NG 3. According to the general procedure, N-graphene (4.7 mg), K_2CO_3 (110 mg, 0.8 mmol), TBAB (516 mg, 1.6 mmol) and 4-(trifluoromethyl) benzyl bromide (940 mg, 3.94 mmol) afforded 13 mg.

Synthesis of *f*-NG 4. According to the general procedure, N-graphene (2.4 mg), K_2CO_3 (55 mg, 0.4 mmol), TBAB (258 mg, 0.8 mmol) and 5-*p*-(bromomethyl) phenyl)-10,15,20 trimesitylporphirinate Zn (II)[3] (372.4 mg, 0.42 mmol) afforded 6 mg.



Sample	XPS data Cl (%at)
f-**NG 1** with PTC	1.2
f-**NG 1** without PTC	0.9

Figure S1. (left): TGA curves for N-graphene (black) and hybrid *f*-**NG 1** obtained under microwave irradiation without phase transfer catalyst (brown) and with phase transfer catalyst (red); (right): comparative XPS data.

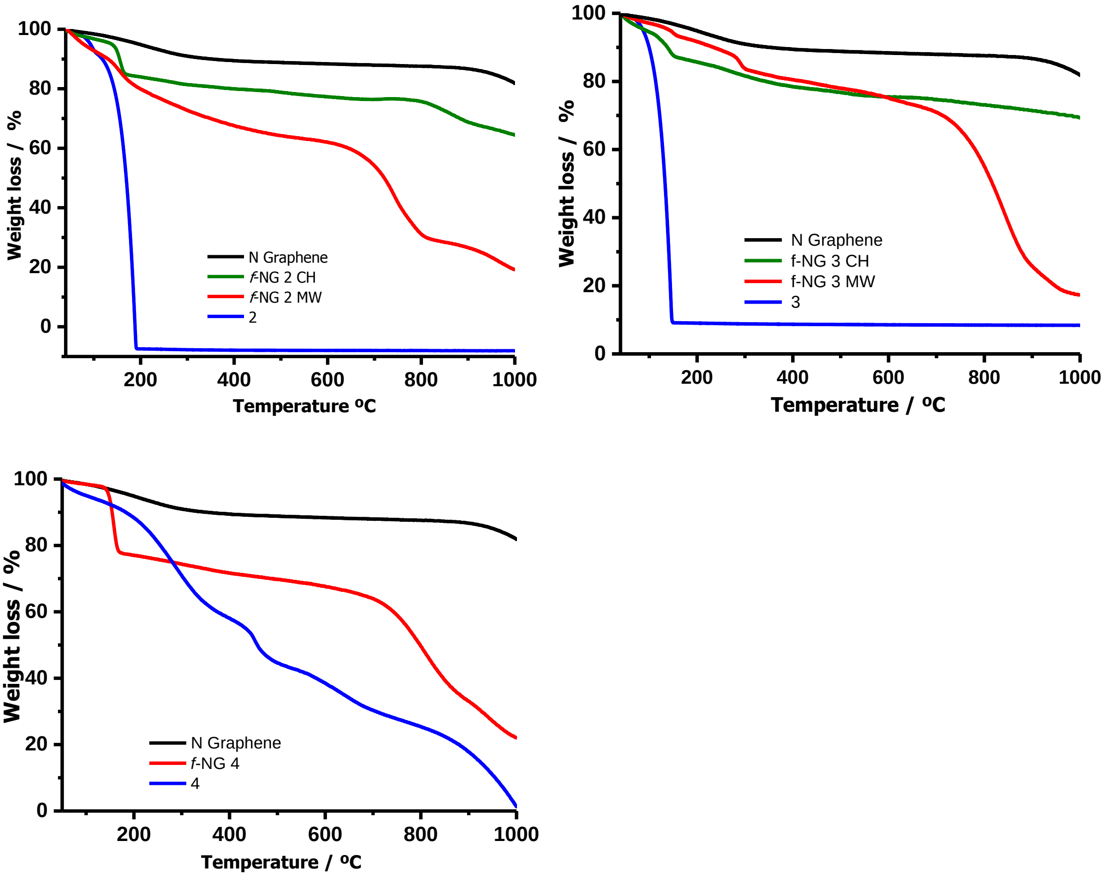


Figure S2. TGA curves for N-graphene (black), hybrids obtained under classical heating (green), hybrids obtained under microwave irradiation (red) and bromide derivatives (blue).

Table S1. Comparative study of the degree of functionalization under classical heating (CH) and microwave irradiation (MW).

Sample	**TGA weight loss (%)**		**Functional group coverage[a]**	
	CH	**MW**	**CH**	**MW**
***f*-NG 1**	12.22	33.12	93	34
***f*-NG 2**	11.07	26.37	90	38
***f*-NG 3**	12.89	13.24	91	88
***f*-NG 4**	-	20	-	295

[a] Number of carbon atoms *per* functional group

Table S2. Binding energies (eV) of core-levels of *f* **NG 1-4** (prepared under microwave irradiation) and its precursor **N(G)**.

	C1s	O1s	N1s	F1s	Cl2p	Zn2p
N(G)	284.8 (62) 286.4 (27) 288.6 (11)	531.6 (35) 532.9 (65)	398.7 (25) 399.8 (54) 401.3 (21)	-	-	
***f*-NG 1**	284.8 (64) 286.6 (27) 288.9 (9)	531.1 (60) 532.9 (40)	398.6 (26) 399.8 (48) 401.4 (26)	-	200.0	
***f*-NG 2**	284.8 (65) 286.6 (29) 288.9 (6)	531.3 (73) 532.8 (27)	398.7 (34) 399.8 (38) 401.4 (28)	-	-	
***f*-NG 3**	284.8 (62) 286.5 (30) 288.4 (8)	530.9 (27) 532.7 (73)	398.7 (29) 399.8 (41) 401.2 (30)	688.0	-	
***f*-NG 4**	284.8 (67) 286.5 (26) 288.9 (7)	530.9 (19) 532.8 (81)	398.7 (35) 399.8 (40) 401.3 (25)	-	-	1021.7

In parentheses are peak percentages

Table S3. Surface atomic composition of functionalized (N)G samples **1-4**, prepared under microwave irradiation, compared with its precursor N(G).

sample	**C (%at)**	**O (%at)**	**N (%at)**	**X (%at)**	**Zn(%at)**
N(G)	96.0	3.4	0.6	-	-
***f*-NG 1**	93.7	4.6	0.7	1.0	-
***f*-NG 2**	92.8	6.6	0.6	-	-
***f*-NG 3**	93.2	4.0	0.7	2.0	-
***f*-NG 4**	94.3	3.6	1.8	-	0.3

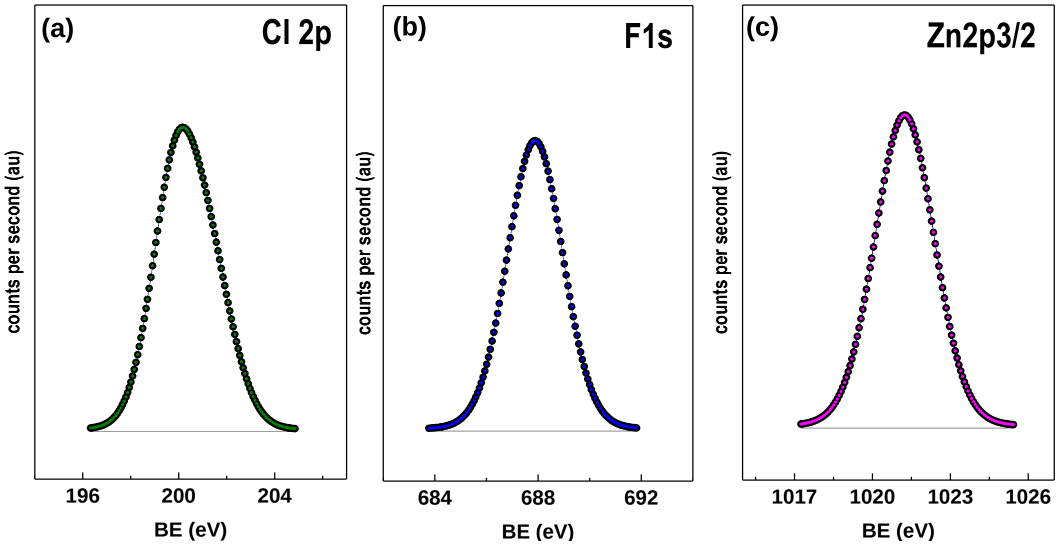


Figure S3. XPS high-resolution spectrum (a) the Cl 1s region of *f*-NG **1** (b) F 1s is region of *f*-NG **3** and (c) Zn2p3/2 region of *f*-NG **4**.

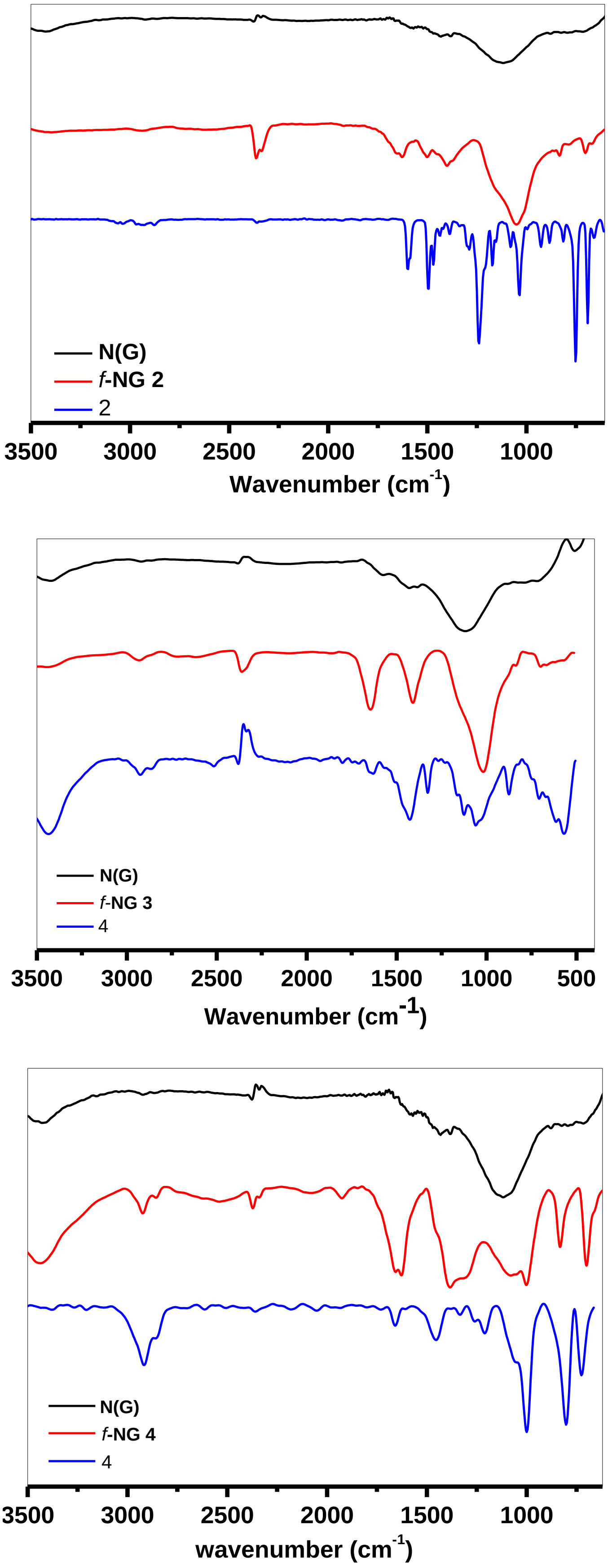


Figure S4. FT-IR spectra of **N(G)** compared to that of the final hybrids **1-4.**

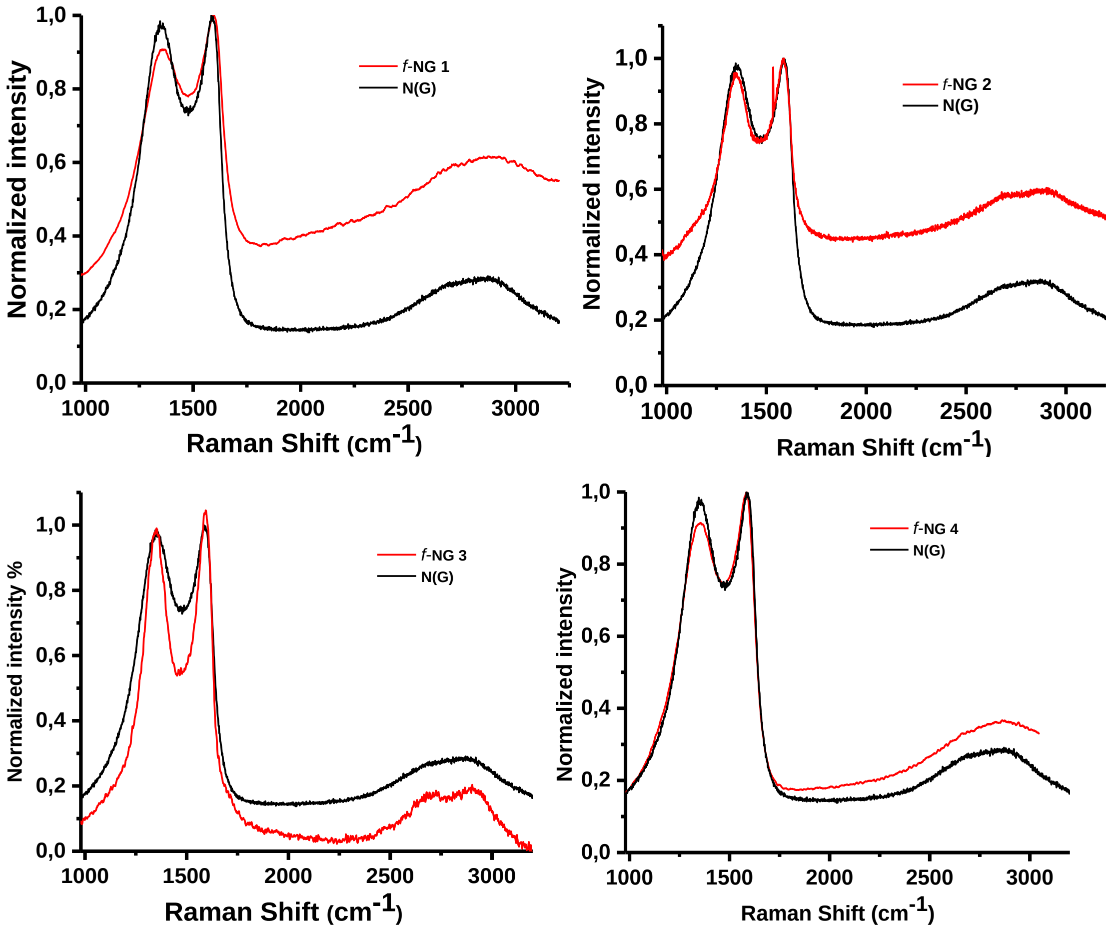


Figure S5. Raman spectra of **N(G)** compared to that of the final hybrids **1-4.**

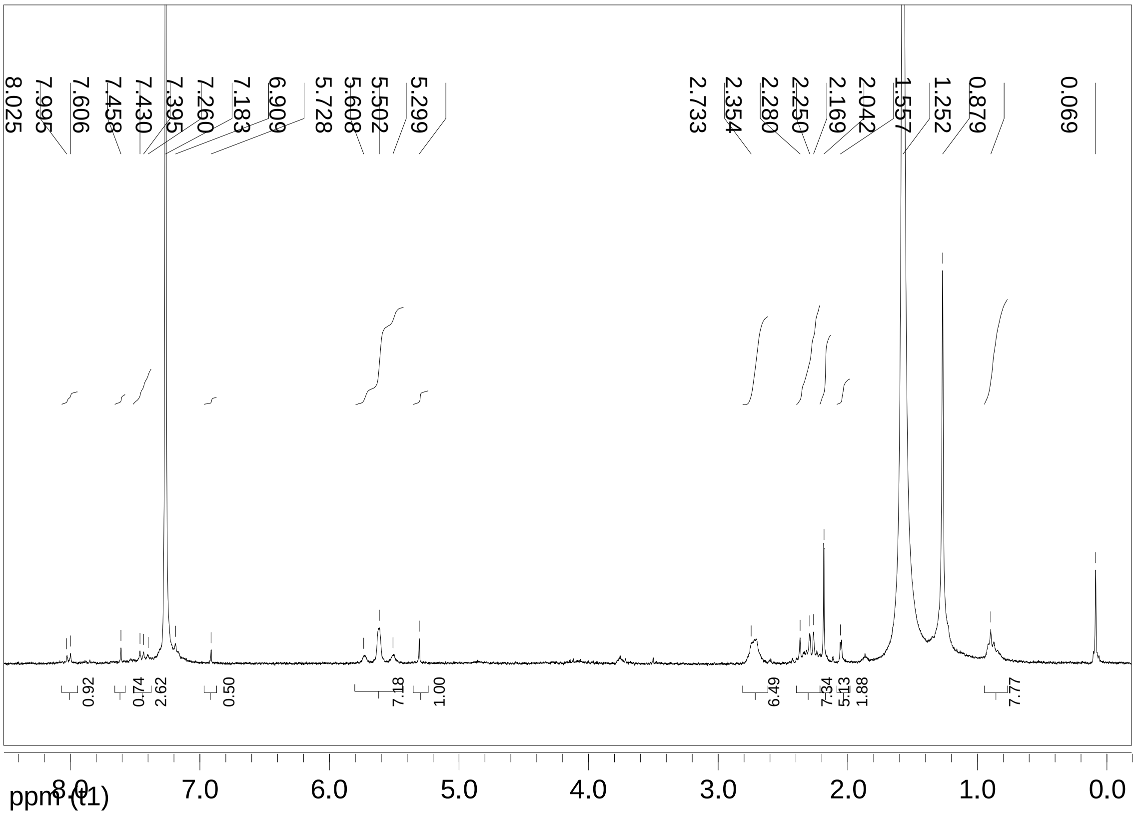


Figure S6. Full ^{1}H-NMR spectrum for ***f*-NG 1.**

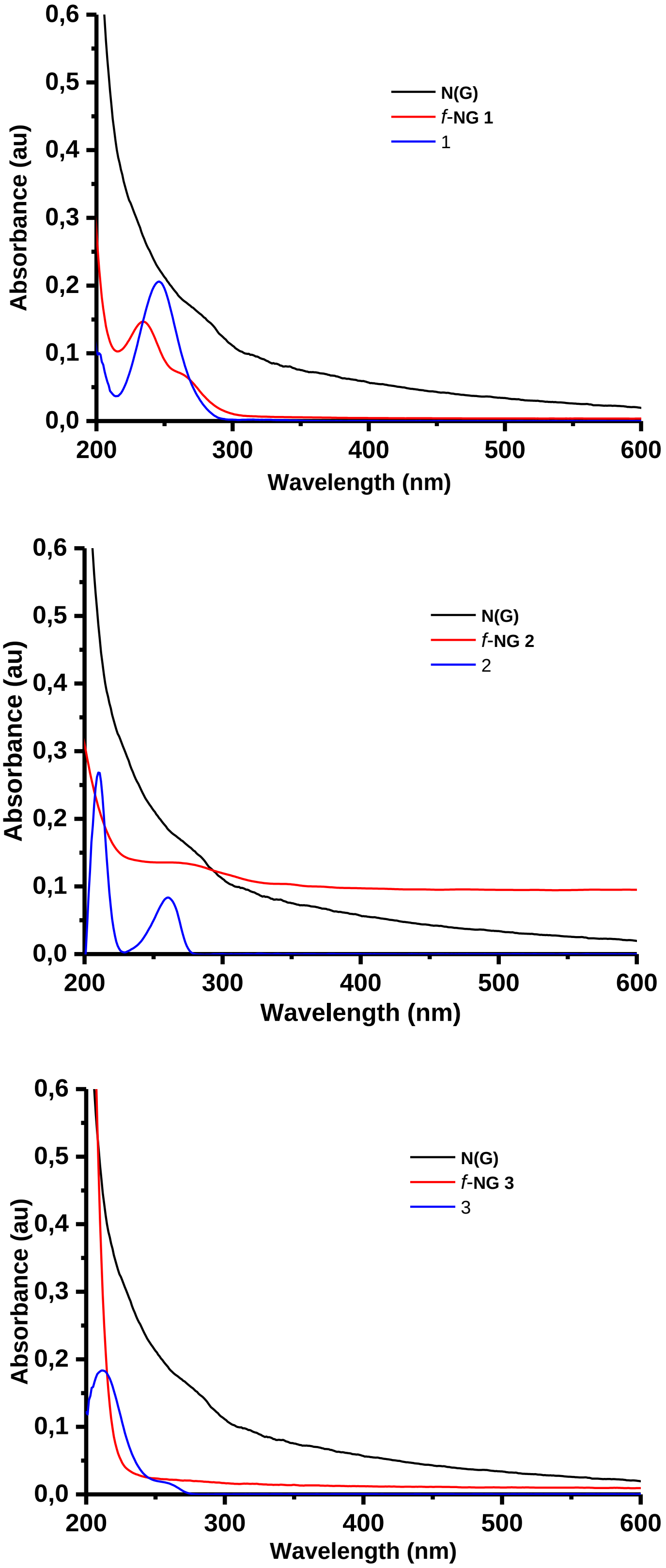
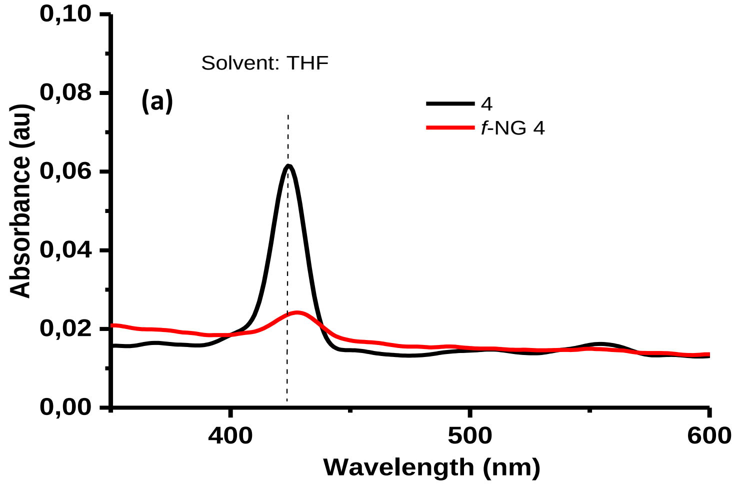


Figure S7. UV-visible absorption spectra (recorded in water) of the starting **(N)G** compared to the final hybrids.



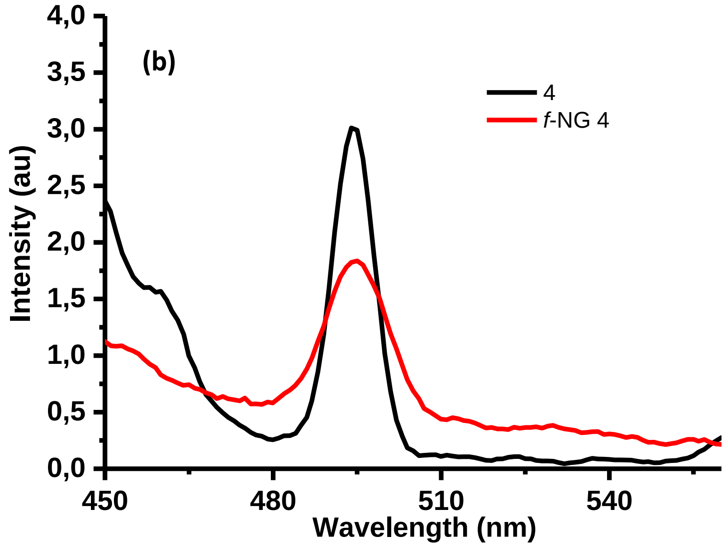


Figure S8. (a) UV-visible absorption spectrum of *f*-**NG 4** and (b) corresponding fluorescence emission spectrum upon excitation at 426 nm.

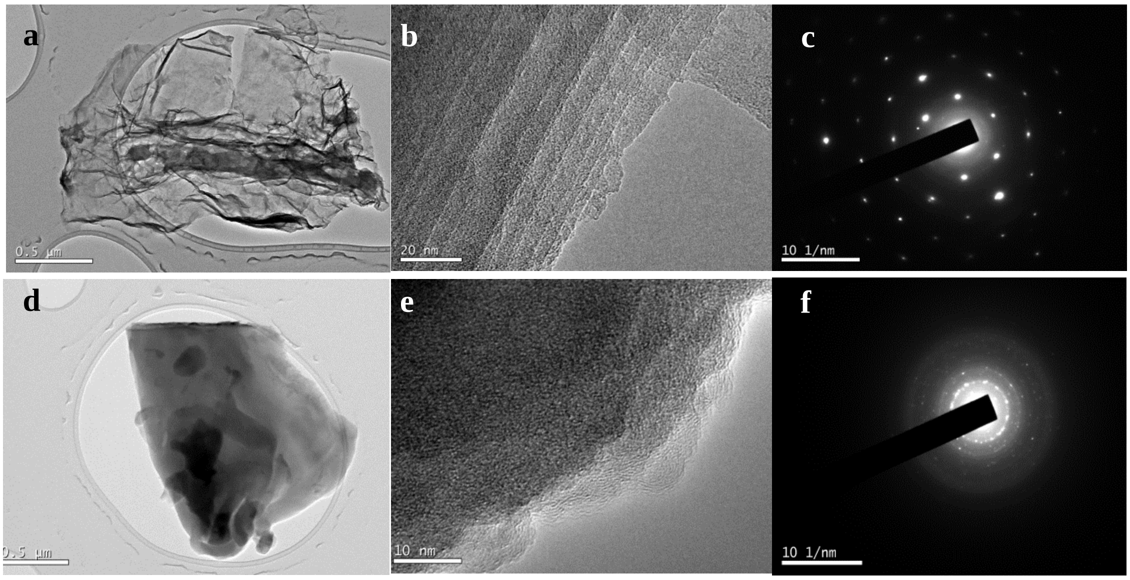


Figure S9. (a,b)TEM images of N-graphene at different magnifications and (c) corresponding SAED pattern and (d, e) TEM images of *f*-**NG 4** at different magnifications and (f) corresponding SAED pattern.

References:

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