Electronic Supporting Information (ESI) for:

Positive Graphene by Chemical Design: Tuning Supramolecular Strategies for Functional Surfaces.

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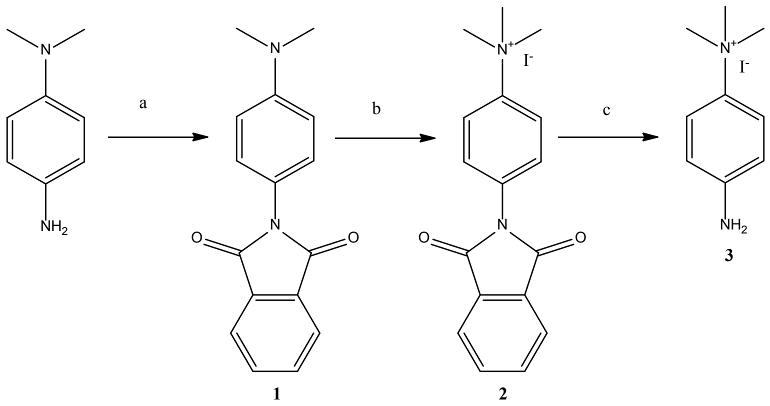
1. Generalities

Chemicals. All reagents and solvents were used as received or purified using standard procedures. **Instruments:** The NMR experiments were performed on a Varian Gemini (200 MHz) NMR spectrometer (proton frequency: 200 MHz; carbon frequency: 50 MHz). ESIMS(+) spectra were collected with a Bruker Model Esquire 4000 instrument. TGA was recorded on a TGA Q500 (TA instruments), under N_2, by equilibrating at 100 °C, and following a ramp at 10 °C/min up to 1000 °C (approximately 1 mg of each compound). Raman spectra were recorded with an Invia Renishaw microspectrometer (100x) and a laser source at 532 nm. TEM measurements were performed on a TEM Philips EM208, using an accelerating voltage of 100kV. Samples were prepared by drop casting from a dispersion onto a TEM grid (200 mesh, nickel, carbon only). Infrared analysis were performed using a Fourier-transform infrared (FT-IR) spectrometer (Perkin-Elmer 2000) by the method of KBr pellets. Melting point were performed on a Büchi SMP-20. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a monochromatic Al KR X-ray (hv = 1486.6 eV) source with a highly focused beam size that can be set from 10 to 300 μm. The beam size used was 200 μm. The energy resolution was 0.6 eV. For the compensation of the built up charge on the sample surface during the measurements, a dual beam charge neutralization composed of an electron gun (~1 eV) and the argon ion gun (~10 eV) was used. For the XPS analysis the samples were supported on a copper tape. The copper tape was completely covered by the graphene sample (powder) so no Cu signal could be recorded. The total covering of the tape by the graphene flakes was verified using an optical microscope; the copper signal in the XPS was used to double check the thickness of the deposition. Binding energies were referenced to the Au 4f7/2 core level. The gold reference is attached to the copper tape used to support the graphene. The dual charge neutralization is used in all measurements performed in the PHY XPS (conducting, semiconducting or insulating powders sample), the gold peak is calibrated to be at 84 eV.

Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian-Lorentzian functions. The photoemission peak areas of each element, used to estimate the amount of each species on the surface, were normalized by the sensitivity factors of each element tabulated for the spectrometer used.

2. Synthesis



Scheme S1. Synthesis of 4-amino-*N,N,N*-trimethylbenzene ammonium, iodide (3). Reagents and conditions: a) Phthalic anhy., Et_3N, toluene, Dean Stark, Δ, o.n.; b) CH_3I, $CHCl_3$, 50°C, 24h, pyrex; c) $N_2H_4.H_2O$, EtOH, r.t., o.n.

2-(4-(dimethylamino)phenyl)isoindoline-1,3-dione (1).

In a Dean-Stark apparatus, 4.0 g of *N,N*-dimethylbenzene-1,4-diamine (29.4 mmol), 8.7 g of phthalic anhydride (58.7 mmol) and 2 mL of Et_3N in toluene (100 mL) were stirred and heated at 130 °C overnight. The mixture was cooling down and solvents evaporated under reduced pressure to 20 mL. The precipitation of the product is observed and the resulting solid was filtered and washed several times with cold toluene, MeOH and Et_2O to give **1** as a yellow solid (7.1 g, 91 %). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.00 (s, 6H), 6.82 (d, 2H, *J* = 9 Hz), 7.25 (d, 2H, *J* = 9 Hz), 7.70-7.80 (m, 2H), 7.81-8.00 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.9 (CH_3), 112.8 (CH), 123.7 (CH and C), 127.7 (CH), 132.1 (C), 134.3 (CH), 150.3 (C), 168.0 (C). IR (KBr pellet) ν 726, 809, 881, 1106, 1186, 1228, 1358, 1393, 1523, 1609, 1706, 3470 cm^{-1}. MS (ESI) *m*/*z* calcd for $C_{16}H_{14}N_2O_2$ 266.1, found *m*/*z* 267.0 $[M+H]^+$. Mp = 260-262°C.

4-(1,3-dioxoisoindolin-2-yl)-*N,N,N*-trimethylbenzenaminium, iodide (2).

In a pyrex tube, 6 mL of CH_3I (96.4 mmol) were added to a solution of **1** (6.0 g, 22.5 mmol) in $CHCl_3$ (100 mL). The mixture was heated at 50°C for 24h and during the reaction, compound **2** precipitated. The solid is filtered and washed with cold $CHCl_3$ and Et_2O to give **2** as a white solid (5.9 g, 64 %). ^{1}H NMR (200 MHz, DMSO-d6) δ 3.70 (s, 9H), 7.74 (d, 2H, *J* = 9 Hz), 7.80-8.10 (m, 4H), 8.18 (d, 2H, *J* = 9 Hz). ^{13}C NMR (50 MHz, DMSO-d6) δ 56.5 (CH_3), 121.4 (CH), 123.5 (CH), 128.3 (CH), 131.3

(CH), 133.1 (C), 134.8 (CH), 146.0 (C), 166.5 (C). IR (KBr pellet) ν 716, 879, 1059, 1230, 1364, 1512, 1609, 1710, 3439 cm^{-1}. MS (ESI) *m*/*z* calcd for $C_{17}H_{17}N_2O_2I$ 408.03, found *m*/*z* 281.1 $[M-I]^+$. Mp = 262-264°C.

4-amino-*N,N,N*-trimethylbenzene ammonium, iodide (3).

3 mL of hydrazine monohydrate (58.9 mmol) were added to a suspension of **2** (5.5 g, 13.5 mmol) in EtOH (20 mL). The mixture was stirred for 24 h at room temperature and filtered. The filtrate, containing the final product, was then evaporated under reduced pressure. The resulting solid was recrystallized with EtOH to give **3** as a beige solid (2.5 g, 69 %). ^{1}H NMR (200 MHz, DMSO-d6) δ 3.48 (s, 9H), 5.63 (s, 2H), 6.64 (d, 2H, $J = 9$ Hz), 7.54 (d, 2H, $J = 9$ Hz). ^{13}C NMR (50 MHz, DMSO-d6) δ 56.5 (CH_3), 113.2 (CH), 120.8 (CH), 135.6 (C), 149.7 (C). IR (KBr pellet) ν 826, 1310, 1514, 1606, 1626, 1659, 3199, 3302, 3378 cm^{-1}. MS (ESI) *m*/*z* calcd for $C_9H_{15}N_2I$ 270.13, found *m*/*z* 151.0$[M-I]^+$. Mp = 203-205°C.[1]

Exfoliated Graphene in DMF (FLG).

Exfoliated graphene (c = 0.3 mg/mL) were prepared by adding 1 g of powdered graphite (grade SP1, batch N°04100, lot N°011705) to 200 mL of DMF (spectroscopic grade, Aldrich). This dispersions was then sonicated (Branson 2510 bath sonicator) for 5 h at 20 °C.

In order to increase the concentration of FLG in the dispersion, two sonication treatments were applied: (a) 5 h ultrasonication followed by the centrifugation of the dispersion (30 min at 3000 rpm) and (b) the further ultrasonication of the supernatant for 1 h after the removal of the larger particles by centrifugation (90 min at 3000 rpm). After sonication, the dispersion was transferred to vials and centrifuged at 3000 rpm for 30 min (HETTICH Zentrifugen, Universal 320, 500–9000 rpm). After centrifugation, the top was carefully removed and allowed to sonication for 1 h at 20 °C and then centrifuged 3 times at 3000 rpm for 30 min removing the precipitate between each cycle. The top (c = 0.3 mg/mL) was carefully removed and retained for further use.

Functionalization of graphene (*f*-FLG).

4-amino-*N,N,N*-trimethylbenzene ammonium (**3**) (217 mg, 1.43 mmol, 2.15 eq.) and 3 mL of H_2O MQ were added to 15 mL of exfoliated graphene (c = 0.3 mg/mL, 1 eq.) under stirring. 3-methylbutyl nitrite (270μL, 1.43 mmol, 5 eq.) was added and the reaction mixture was immediately heated at 80 °C overnight. After cooling to room temperature, the suspension was diluted with DMF (100 mL) and filtered over a PTFE (0.45mm, Omnipore JHWP, Millipore) membrane. The solid recovered on the filter was dispersed in DMF (100 mL), sonicated for 10 min in a water bath, and filtered over an PTFE (0.45 mm, Omnipore JHWP, Millipore) membrane. This sequence was repeated twice with DMF, methanol, dichloromethane, and diethyl ether.

Non-covalent interaction with POM (Ru_4POM@*f*-FLG).

1 mg of functionalized graphene were added to an aqueous solution of POM (10^{-4} mol/L, 2 mL) at pH 4. The mixture was sonicated for 2 min and let under stirring overnight. The suspension was diluted with H_2O MQ at pH 4, filtered over a PTFE (0.45 mm, Omnipore JHWP, Millipore) and the resulting functionalized graphene with POM was washed several time with H_2O MQ (pH 4) and resuspended in 10 mL of H_2O MQ at pH 4

3. ^{1}H and ^{13}C NMR spectra

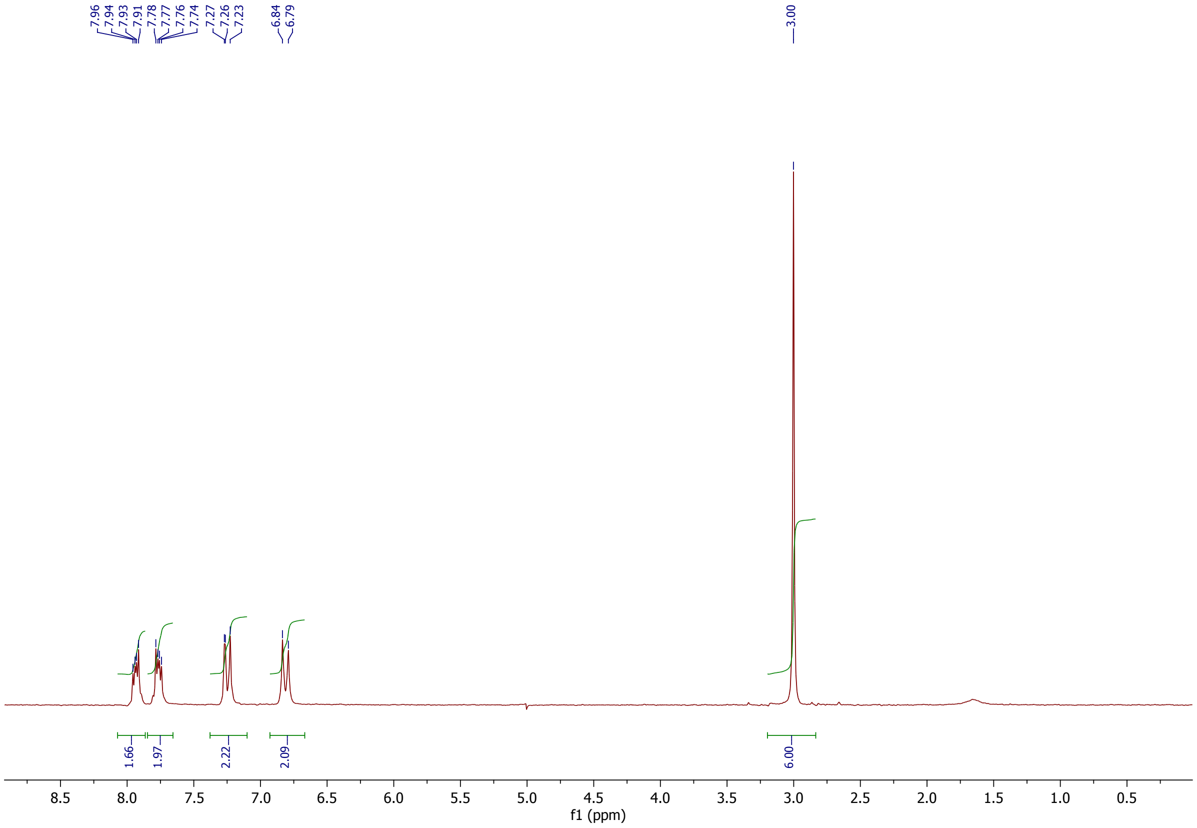


Figure S1. ^{1}H NMR spectrum of 1 in $CDCl_3$.

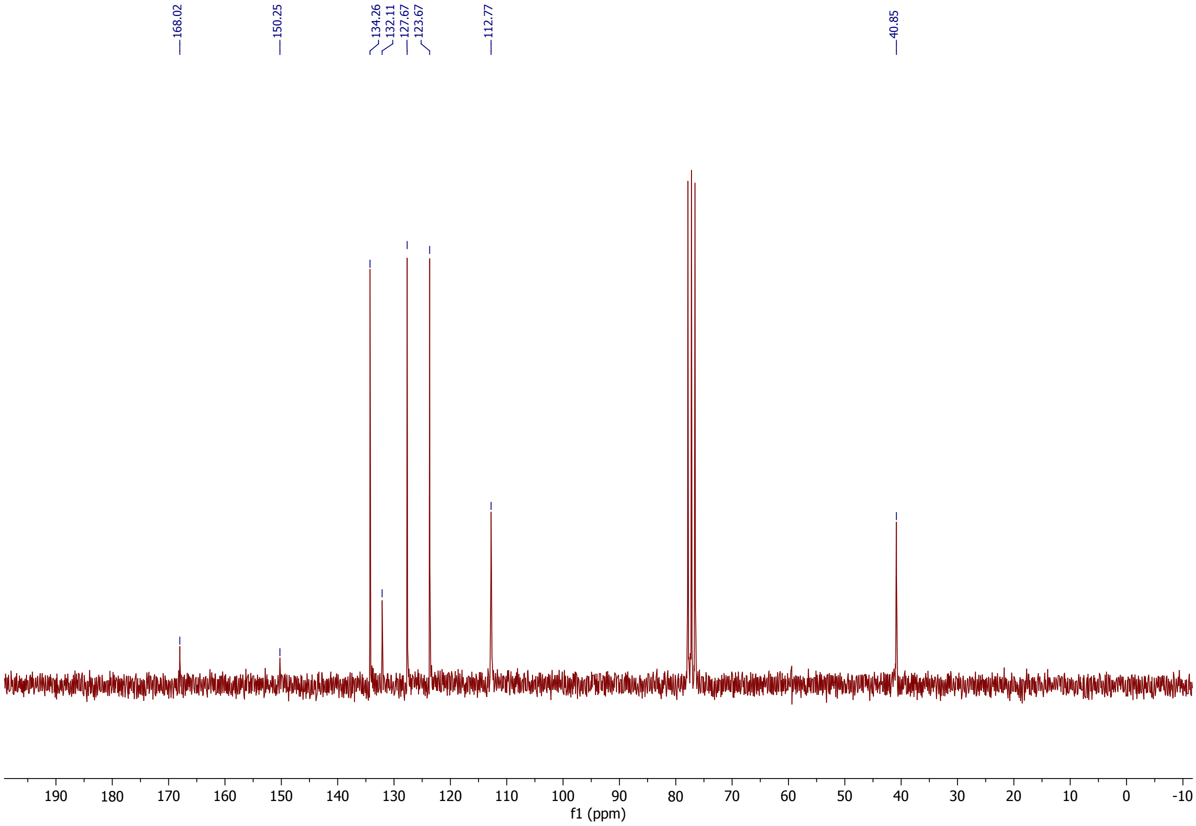


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

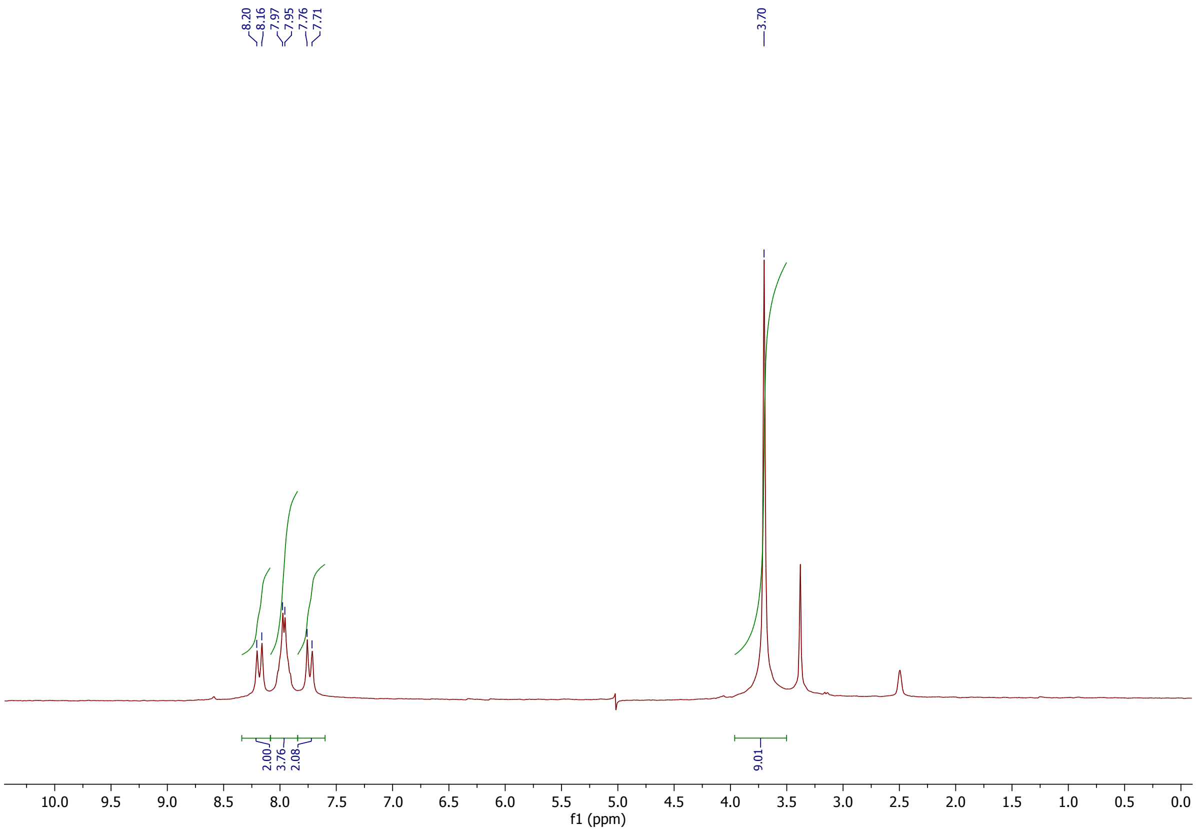


Figure S3. ^{1}H NMR spectrum of **2** in DMSO-d6.

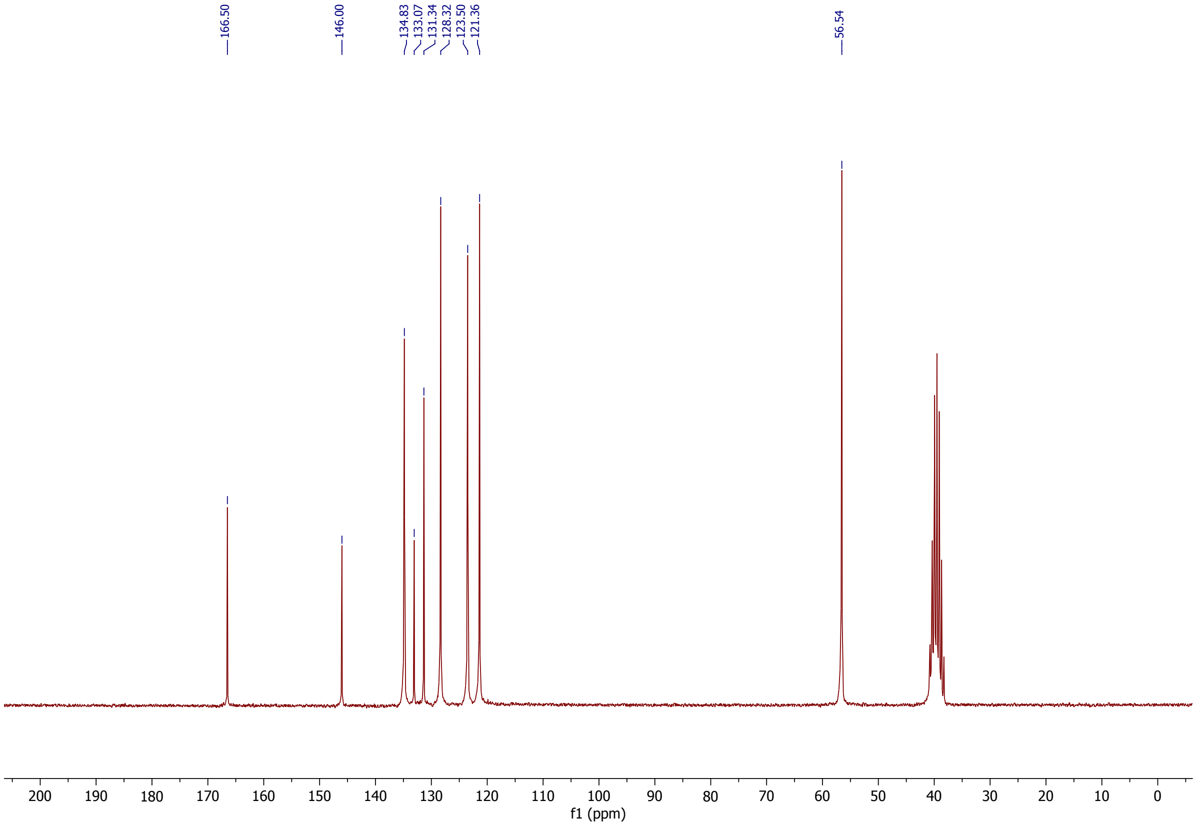


Figure S4. ^{13}C NMR spectrum of 2 in DMSO-d6.

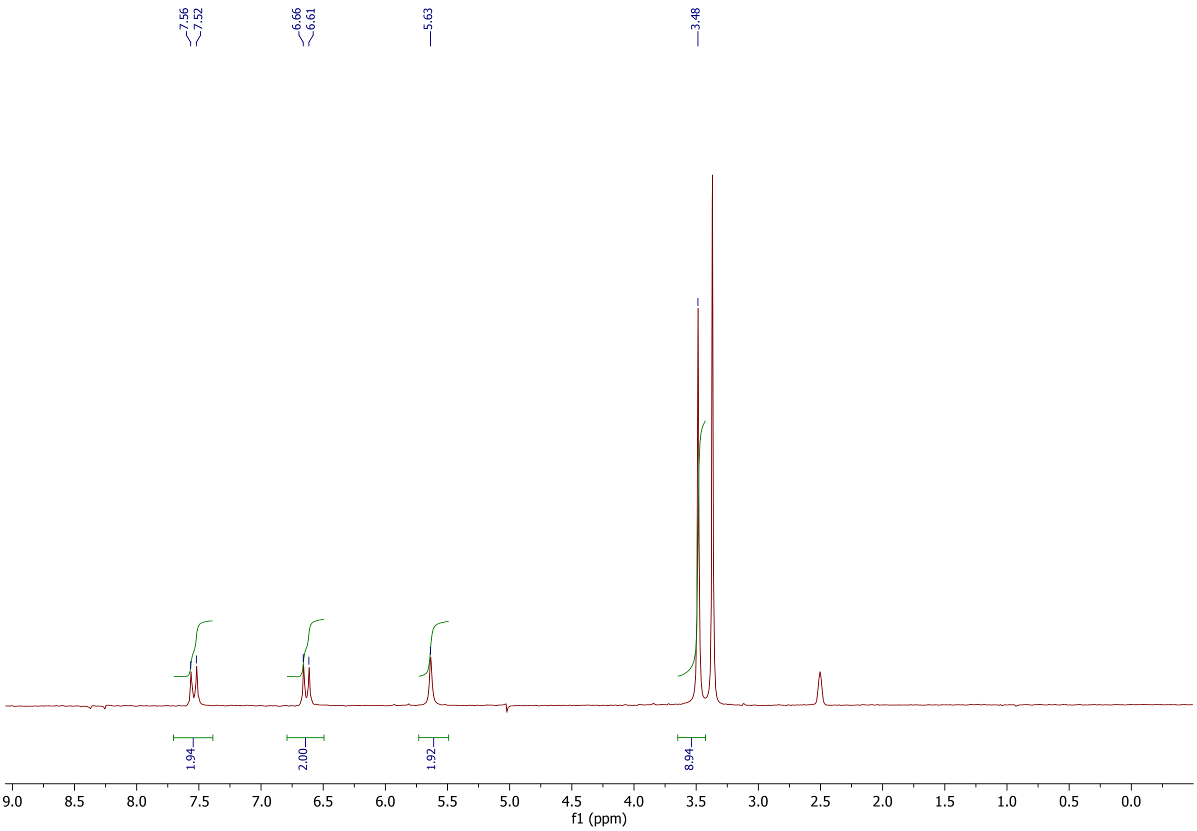


Figure S5. ^{1}H NMR spectrum of 3 in DMSO-d6.

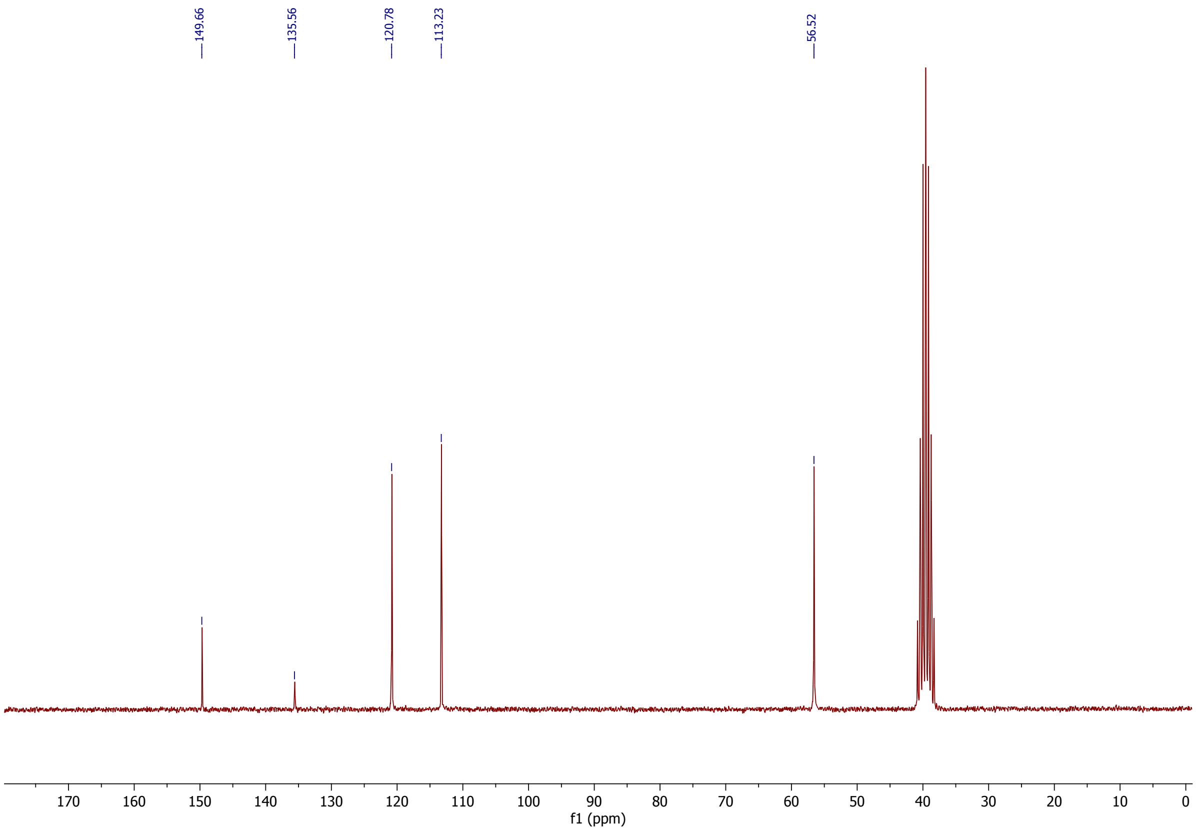


Figure S6. ^{13}C NMR spectrum of 2 in DMSO-d6.

1. ESI-MS spectra

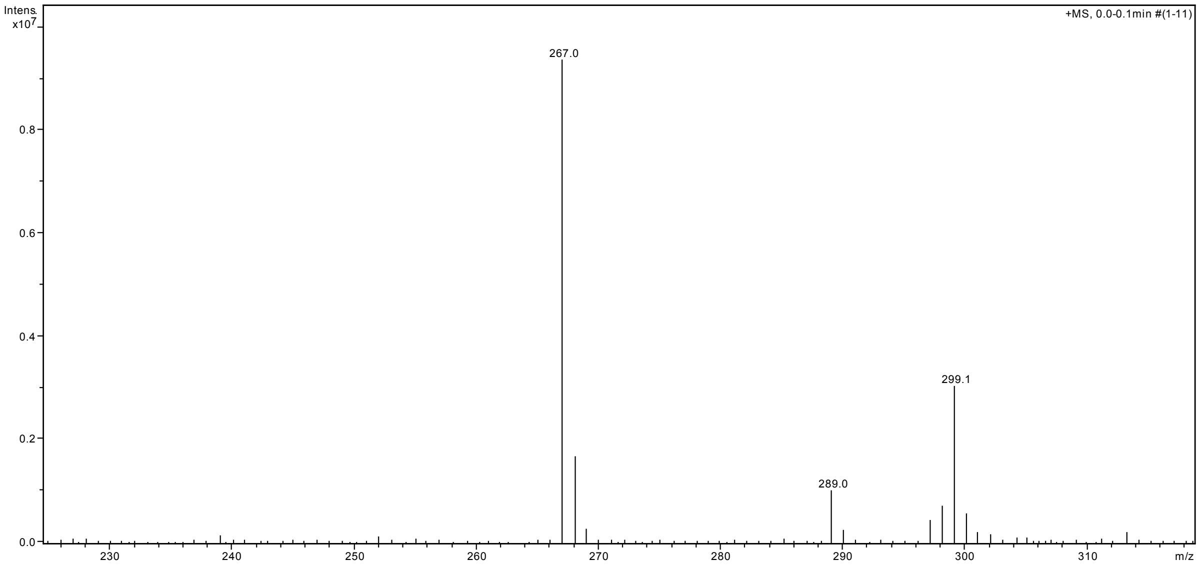


Figure S7. ESI-MS spectrum of 1.

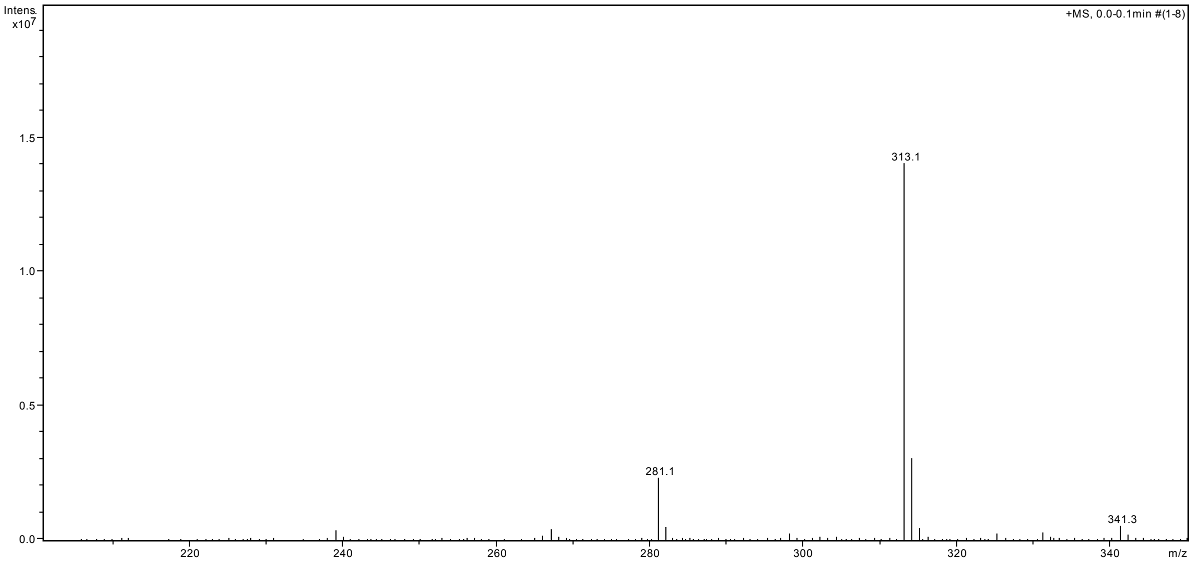


Figure S8. ESI-MS spectrum of 2.

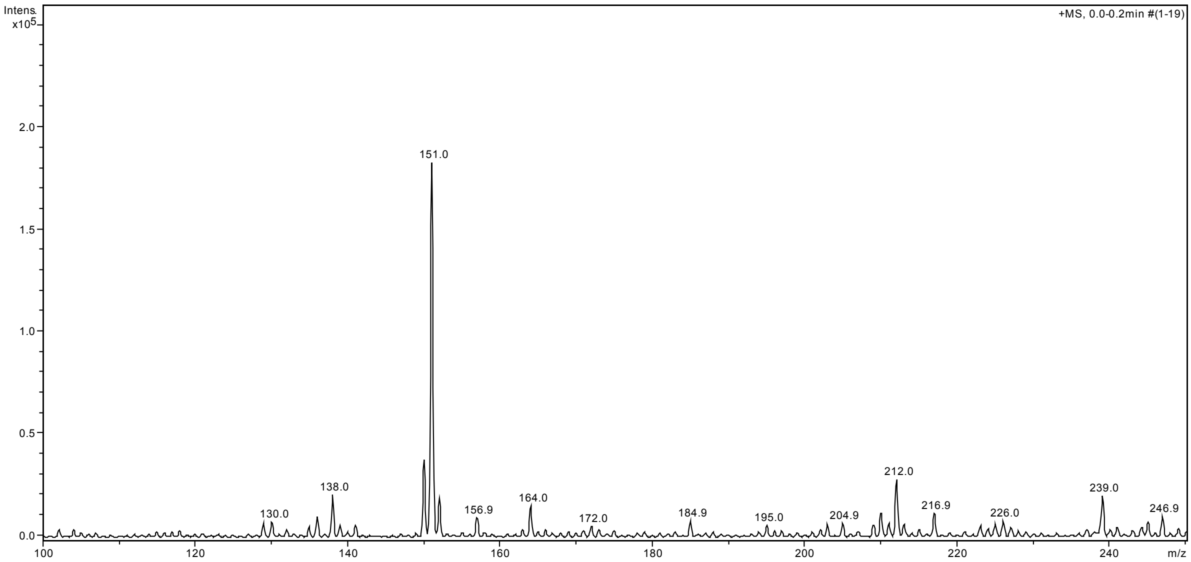


Figure S9. ESI-MS spectrum of 3

2. TGA

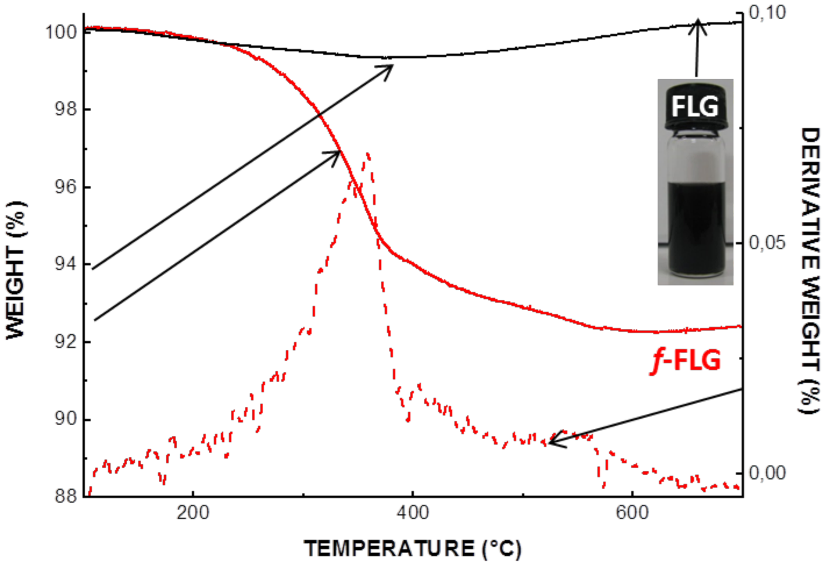


Figure S10. Weight loss plot of FLG and f-FLG (solid) and derivative plot of f-FLG (dotted). Inset: image of FLG in DMF (c = 0.3 mg/mL).

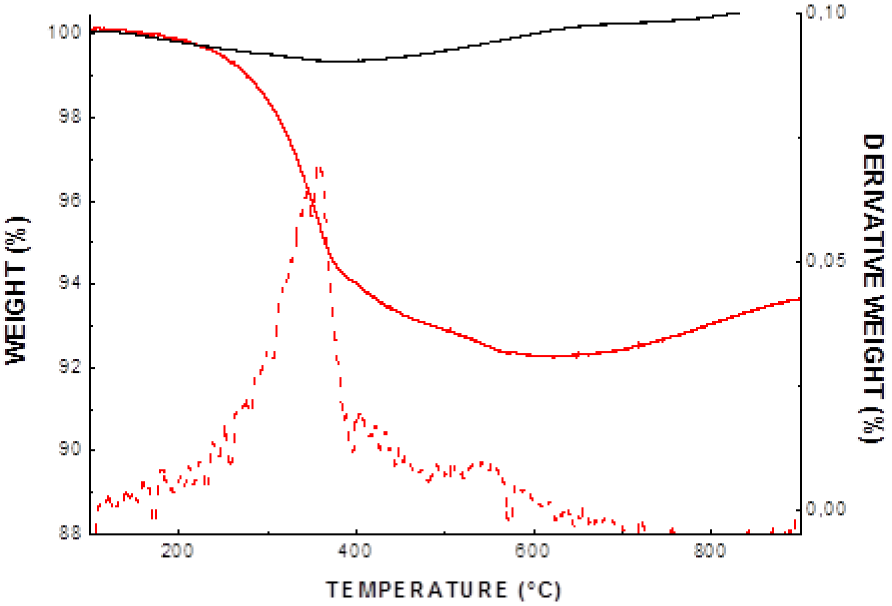


Figure S11. Weight loss plot of FLG and f-FLG (solid) and derivative plot of f-FLG (dotted) until 900°C.

3. Raman spectroscopy

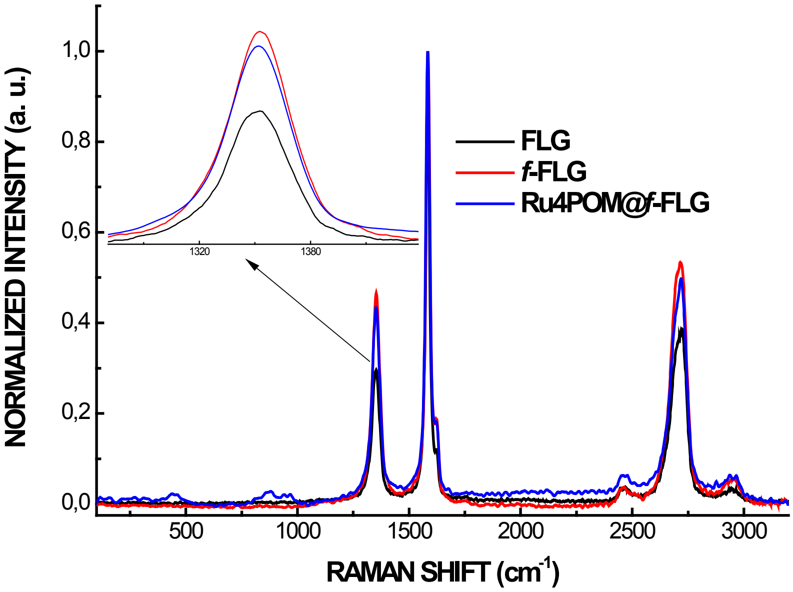


Figure S12. Raman spectra of FLG (black curve), *f*-FLG (red curve), and Ru_4POM@*f*-FLG (blue curve) with a laser intensity at 532 nm. In the inset, the increase of the D band is shown.

4. TEM images

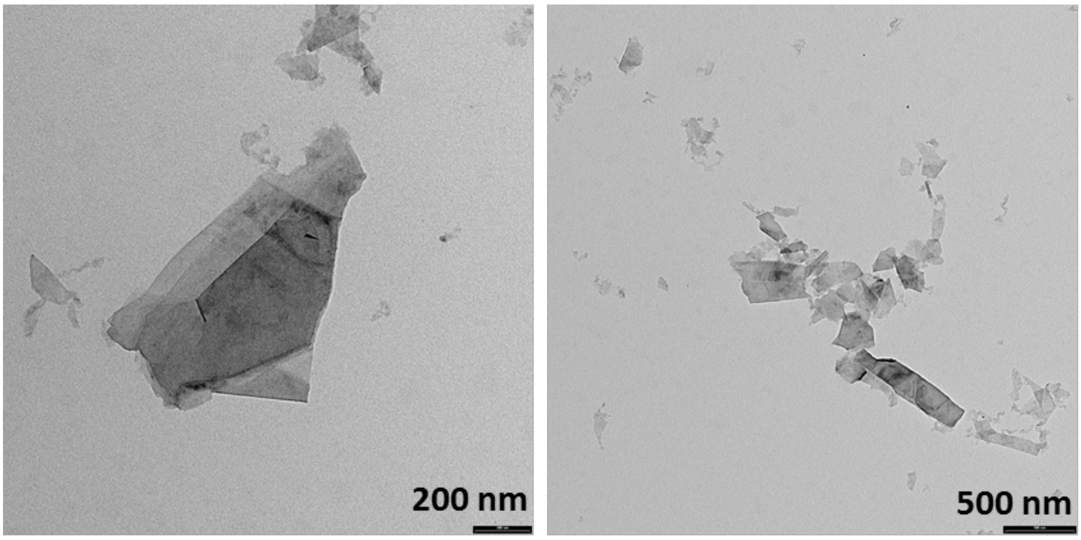


Figure S13. TEM images of FLG in DMF (c = 0.3 mg/mL).

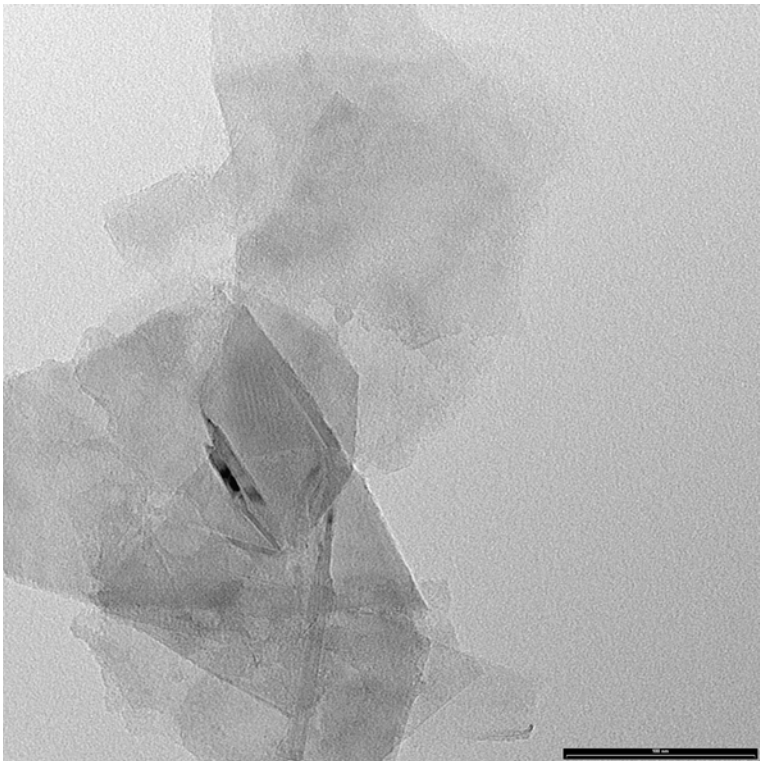


Figure S14. TEM image of *f*-FLG (in DMF).

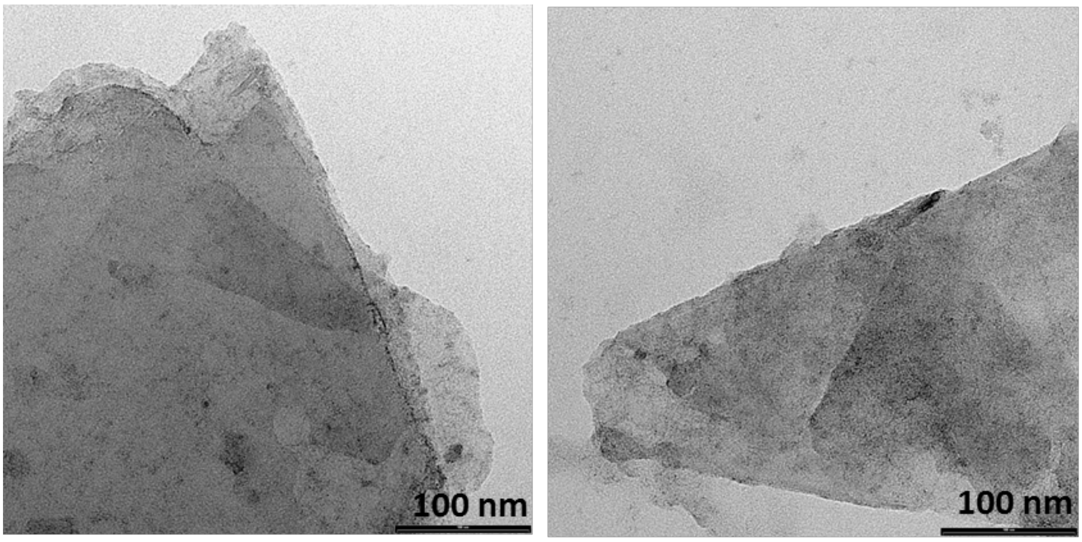


Figure S15. TEM images of Ru_4POM@*f*-FLG (in H_2O MQ pH = 4).

5. X-Ray photoelectron spectroscopy

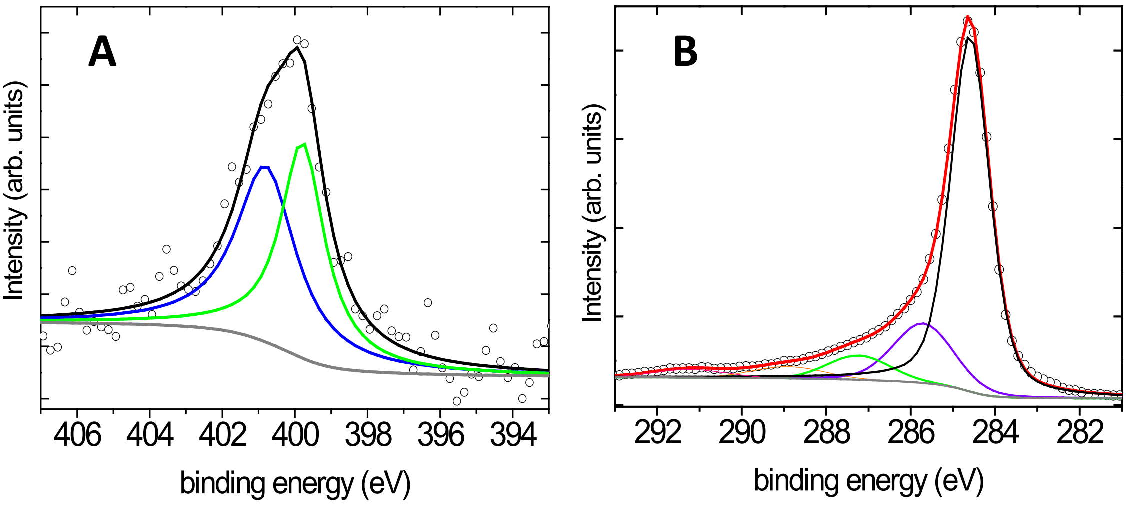


Figure S16. X-Ray photoelectron spectra and fit of the (A) N 1s core level region and (B) C 1s core level region for *f*-FLG.

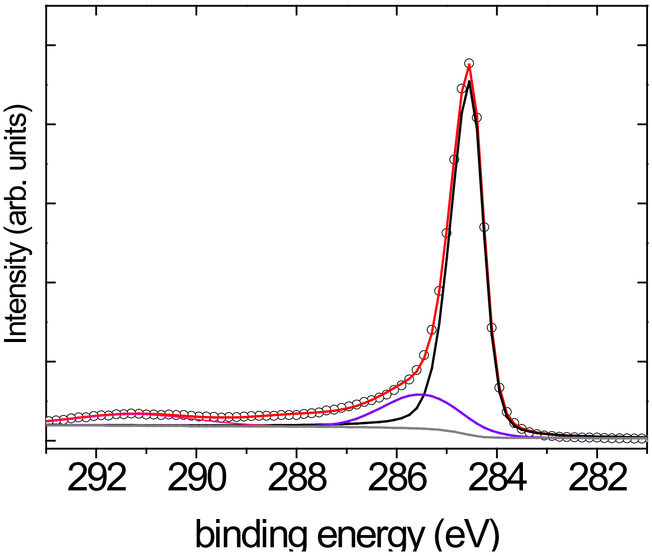


Figure S17. X-Ray photoelectron spectra and fit of the C 1s core level region for FLG.

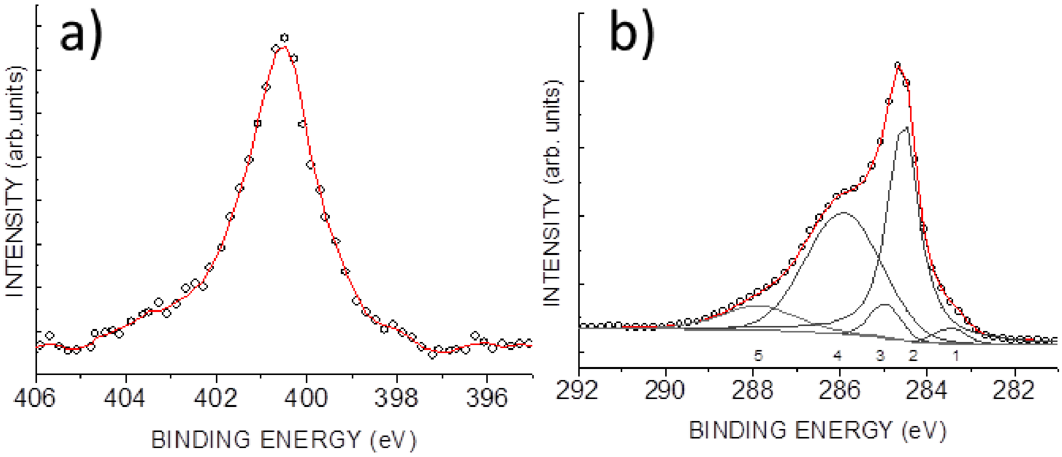


Figure S18. X-Ray photoelectron spectra (a) N 1s core level region (the red line results from a smoothing signal processing) and (b) C 1s core level region for Ru_4POM@*f*-FLG. The grey curves indicate the 5 components used to reproduce the C1s spectrum (red line).

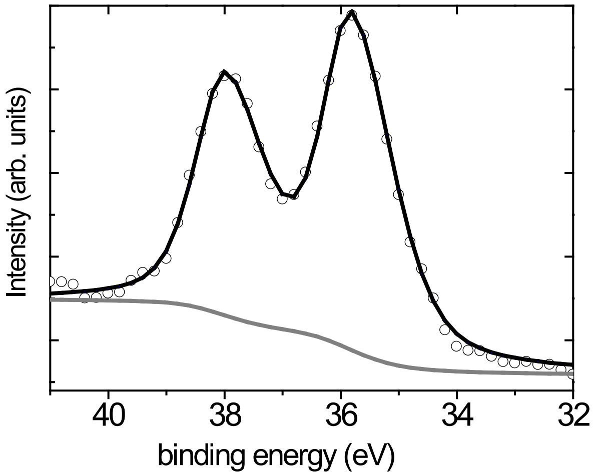


Figure S19. X-Ray photoelectron spectra and fit of the W 4f core level spectrum for Ru_4POM@f-FLG.

6. Catalytic activity

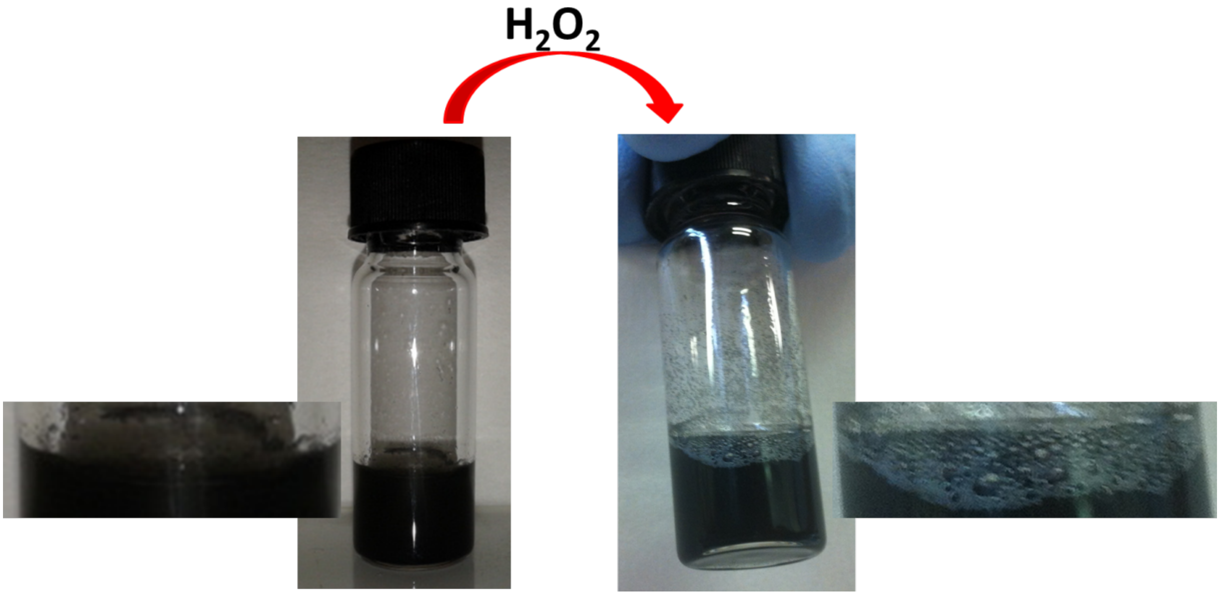


Figure S20. Left, $Ru_4POM@$*f*-FLG in solution in water (1mg/mL). Right $Ru_4POM@$*f*-FLG after addition of H_2O_2 (35% v/v) oxygen evolution can be observed.

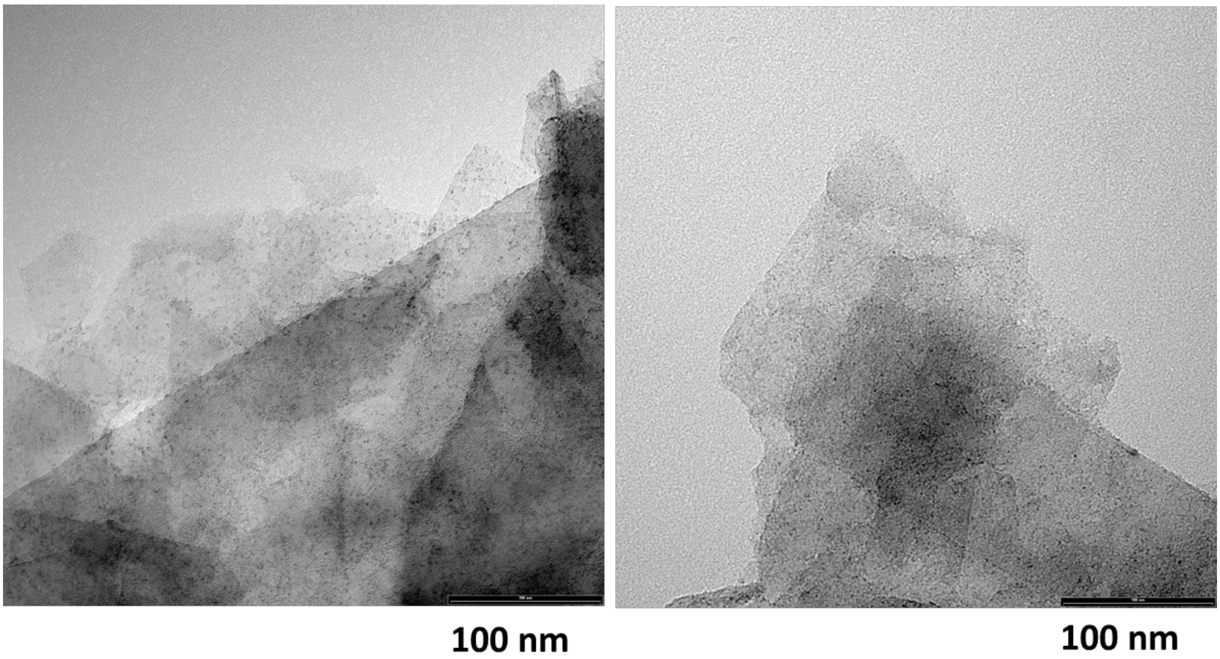


Figure S21. TEM images of $Ru_4POM@$*f*-FLG (in H_2O MQ) recovered after addition of H_2O_2 (35% v/v) showing the inorganic cluster domains well-distributed all over the graphene surface.

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[1] Litt : Mp = 201°C. Minkin, V. I.; *Zhurnal Obshchei Khimii* **1962**, *32*, 1591-7.