

Supporting Information

White light induced covalent modification of graphene using phenazine dye

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Raman spectra acquired from different sample positions. 9

Table 1. Raman D, G, 2D pick positions from multiple points P1-P6 of the mGnP sample

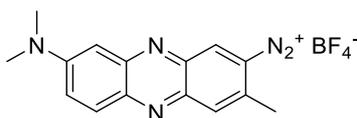
Table 2. Raman D, G, 2D pick positions from multiple points P1-P6 of the untreated GnP sample 9

General

All reagents were obtained from Sigma Aldrich, Alfa Aesar, VWR and Acros and used without further purification. All the reactions were stirred with a magnetic stirrer unless otherwise stated. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV3-400 or a Bruker Advanced 500 spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual solvent peak, and peaks are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qui), sextet (sex), multiplet (m), broad singlet (br), and coupling constants (J) are quoted in Hertz (Hz). Spectra were recorded in deuterated chloroform or deuterated dimethyl sulfoxide and were measured at room temperature unless otherwise stated. Where needed, two dimensional correlation spectroscopy (2D-COSY), heteronuclear single quantum coherence spectroscopy (HSQC) and heteronuclear multiple bond correlation spectroscopy (HMBC) were used in order to aid assignment. High resolution mass spectrometry was performed on Bruker MaXis Impact (EI+) by positive and negative electrospray ionisation. The accepted experimental error is <4 ppm. Infrared spectra (IR) were recorded in solid phase on a Bruker Alpha Platinum ATR FTIR spectrometer with vibrational frequencies given in cm^{-1} . The electronic absorption spectra were recorded on a Cary 100 UV-Vis scanning spectrophotometer. The fluorescence spectra were recorded on a FluoroMax-3 spectrofluorimeter. Light source for photochemical reactions was a nightsearcher workstar SMT LED Portable Rechargeable Floodlight (2200 Lumens per LED, 10 LED station) at a distance of 12 cm from the sample. Dry "composite crystals" were dispersed in ethanol and one drop of suspension was put on silicon wafers, which was mounted on an SEM stub using an adhesive copper film, and samples were viewed, without coating, with a FEI Nova 450 FEG-SEM operating at 3 kV using deceleration mode and CBS detector.

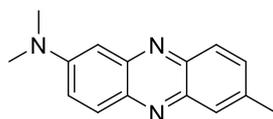
Experimental Methods

Synthesis of 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate



Neutral Red (1.47 g; 5.04 mmol) was dissolved in tetrafluoroboric acid (7 mL; 50 % w/w H₂O) and stirred. A saturated solution of sodium nitrite (0.35 g in 2 mL H₂O; 5.04 mmol) was added dropwise and the reaction was left stirring for 2 hours. A small volume of diethyl ether (5 mL) was added and the diazonium salt was filtered as a purple powder by vacuum filtration. Yield 1.2 g, 68 %. ¹H NMR (500 MHz, CDCl₃) δ_H: 2.64 (3H, s), 3.49 (6H, s), 6.70 (1H, s), 7.67 (1H, d, *J* 10.3), 7.81 (1H, s), 8.02 (1H, s), 8.06 (1H, d, *J* 10.2); ¹³C NMR (101 MHz, CD₃CN) δ_C: 157.1, 145.1, 139.9, 139.4, 138.6, 135.8, 133.7, 129.7, 126.3, 118.07, 91.5, 41.8, 21.4; HRMS *m/z* (ESI⁺) found 341.1759 [C₁₅H₁₄N₅⁺+2H₂O+MeCN], calcd 341.1721, found 238.1339 [C₁₅H₁₅N₃+H⁺] calcd 238.1335; FTIR ν (cm⁻¹): 3565 (N-H), 3358 (N-H), 1620 (C=C aromatic), 1524 (C=C aromatic), 1275 (N-C stretch), 1211 (N-C stretch), 1165 (N-C stretch), 803 (Aromatic C-H bend), 707 (Aromatic C-H bend), 550-518 and 473 (B-F stretch); UV-vis in MeOH λ_{max} (ε) 374 (6658), 532 (10364) nm.

Synthesis of 7-dimethylamino-3-methylphenazine via hydrodediazonation



Phenazine diazonium salt (70 mg; 0.23 mmol) was dissolved in MeOH (5 mL) and sodium nitrite (25 mg; 0.46 mmol) was added. Rapid colour change from purple to red was observed upon stirring. The compound was isolated by evaporation of the solvent. Yield 40.5 mg, 74 %.

Covalent functionalization of graphene (GnP) with 3-methyl-7-dimethylaminophenazinediazonium tetrafluoroborate

Graphene (50 mg) was suspended in a stirred solution of EtOH (100 mL) and phenazine diazonium salt (92 mg, 0.262 mmol). The sample was illuminated with white LED light (40 min) and stirred for 2 hours to ensure reaction went to completion. The purple solution was then filtered and the powder washed with acetone until purple colour was no longer washed out from the powder (3x 15 mL). After this, the solubility of the compound was tested with several solvents, including solvents which would dissolve MDAP. These solvents were toluene, cyclohexane, DMSO, DMF and THF. Out of these solvents, only DMSO and DMF produced coloured solutions after shaking and sonicating (pale orange and dark orange respectively) with powder still remaining, the other solvents remained colourless with black precipitate. Yield 74 mg. IR: 2612 – 2380 cm⁻¹ (broad,), 2154 cm⁻¹ (C-H), 2031 cm⁻¹ (C-H), 1975 cm⁻¹ (C-H), 1588 cm⁻¹ (C=C aromatic), 1070 cm⁻¹ (Car-C or Car-N) and 724 cm⁻¹ (aromatic C-H bend), UV-vis in DMF λ_{max}(nm) 281 and 467. BET analysis results showed a Langmuir surface area of 209.1240 m²/g at 22 °C.

Spectrophotometric monitoring of the covalent functionalization under no illumination (dark) and white light illumination

Typical sample preparation procedure: Graphene (20 mg) was dispersed under stirring in the ethanoic solution (12.5 mL) of the diazonium salt (12.5 mg). Throughout 40 minutes of stirring under either dark or illuminated conditions, an aliquot from the reaction (0.1 mL) was taken every 5 minutes, passed through round 0.4 μm filter and diluted with EtOH (3.4 mL). A UV-vis scan of each sample was recorded between 300-800nm. This was used to determine the concentration at which the maximum number of diazonium molecules had chemically bonded to graphene as well as the rate compared to dark conditions. Reactions uses 54% of the added graphene.

Working concentration range for 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate

To establish the stability and the working concentration range to monitor the reaction, UV-vis data were collected through a range of concentrations (0.026 to 0.085 mM) of free of 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate in EtOH.

Figure 1. The linear plot of the free diazonium salt concentrations and corresponding absorbance at 537 nm in EtOH used in the UV-vis monitoring of the progress of graphene modification

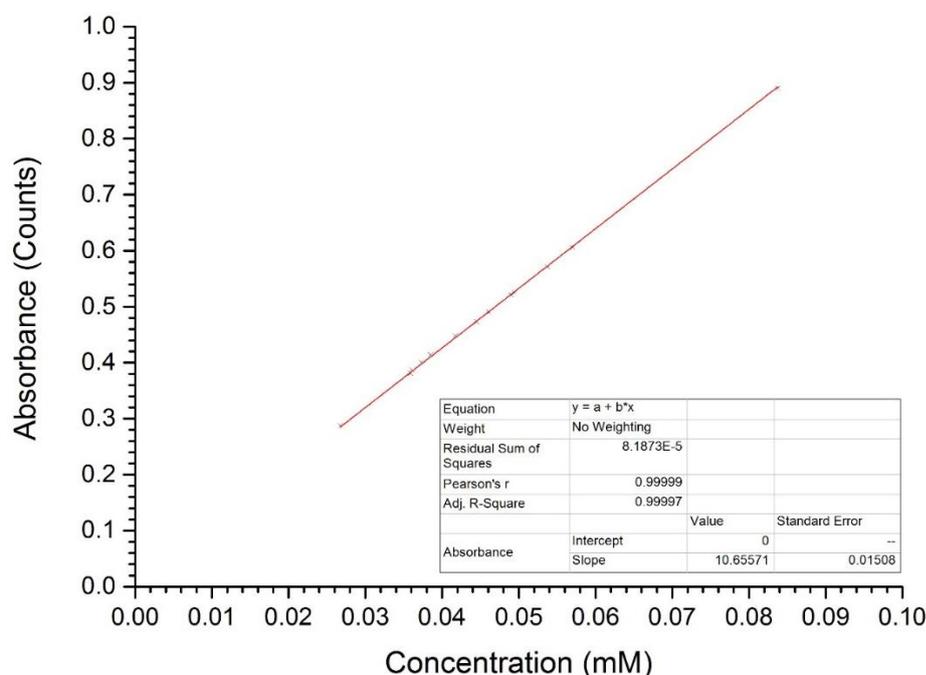


Figure 2. The normalised UV-vis spectrum of diazonium salt in EtOH with a peak at 534 nm.

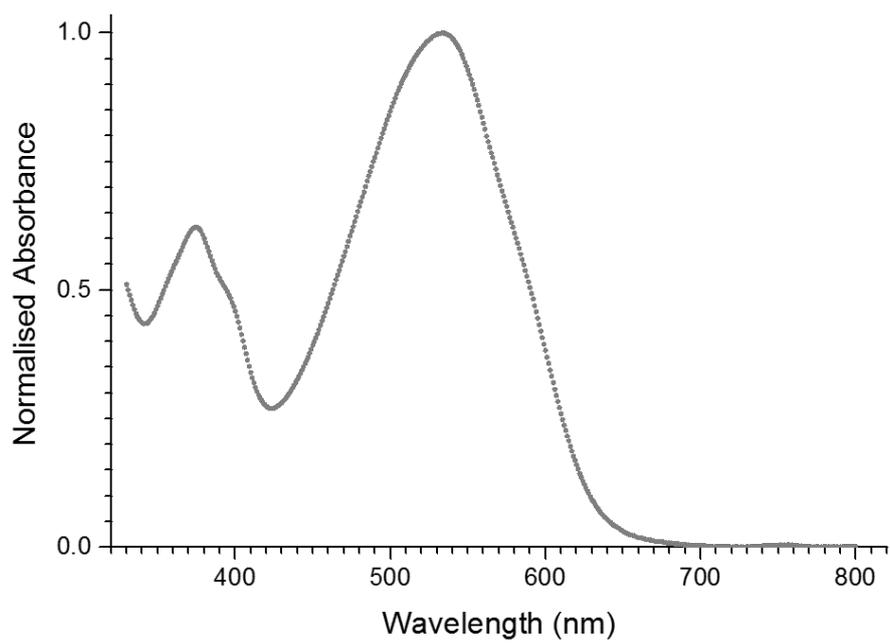


Figure 3. ^1H NMR (CDCl_3 , 500 MHz) of 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate

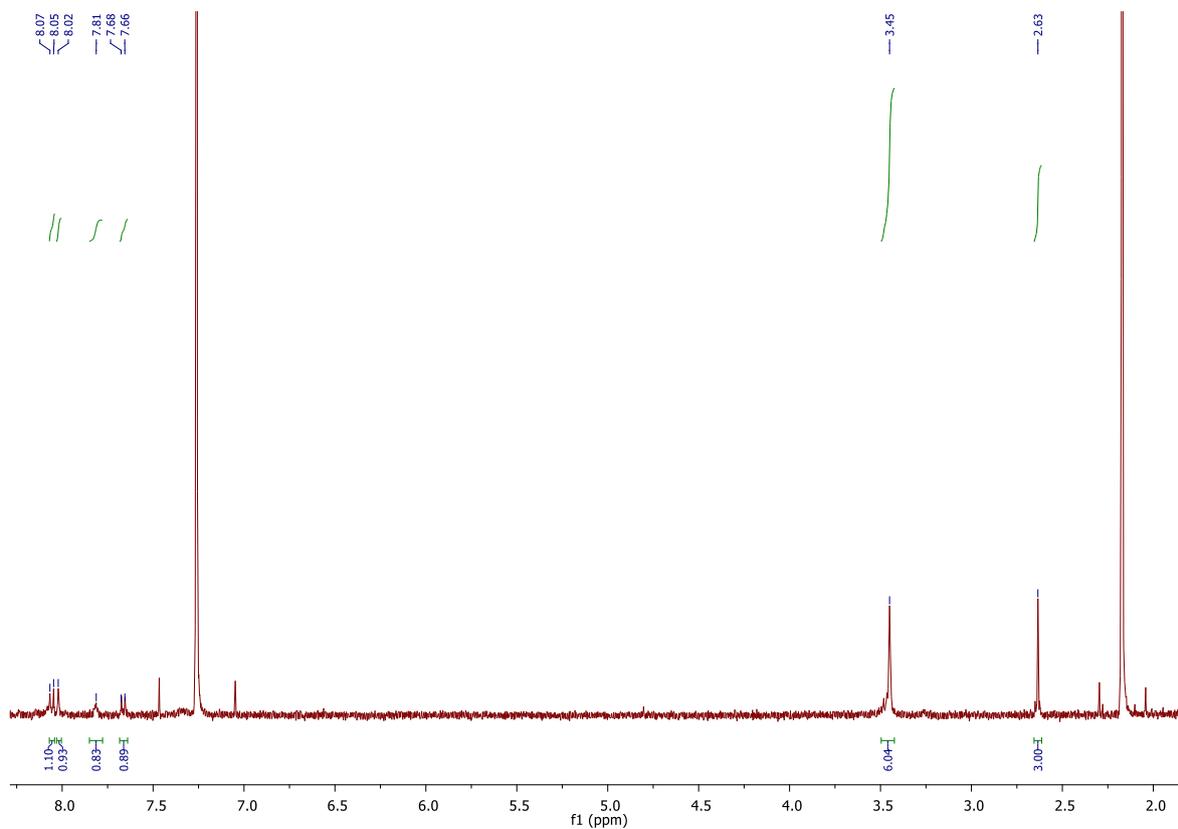


Figure 4. ^{13}C NMR (MeCN-d_3 , 400 MHz) of 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate

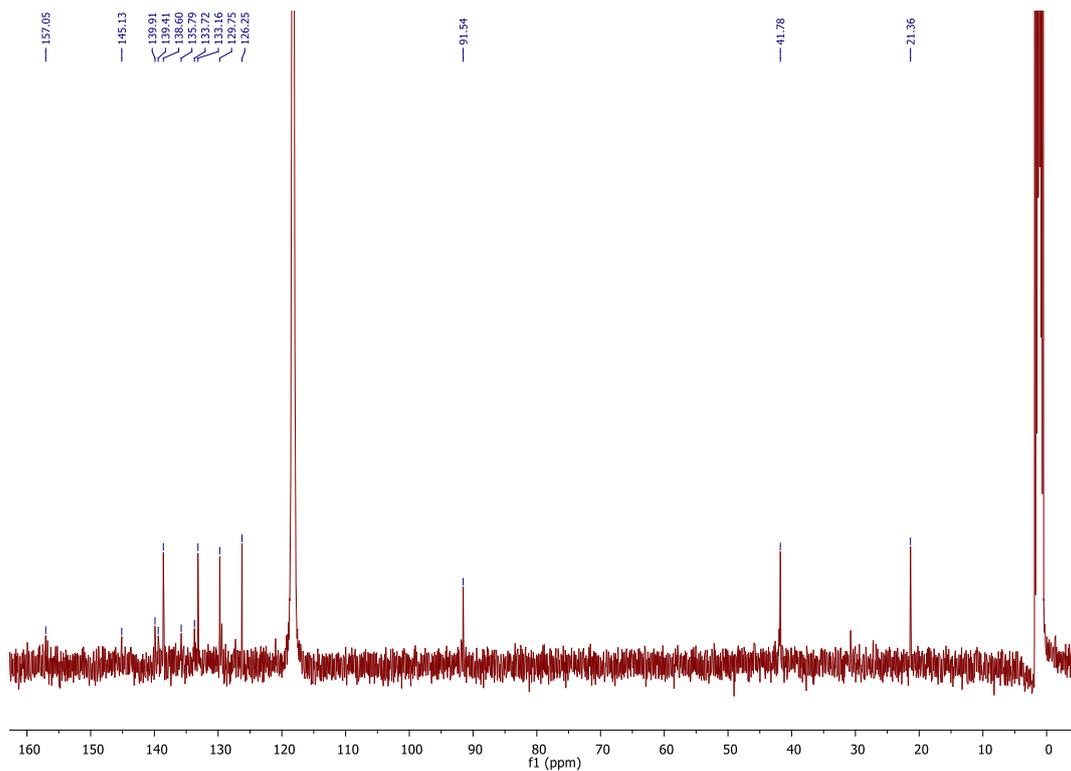


Figure 5. FTIR spectrum of 3-methyl-7-dimethylaminophenazine-2-diazonium tetrafluoroborate

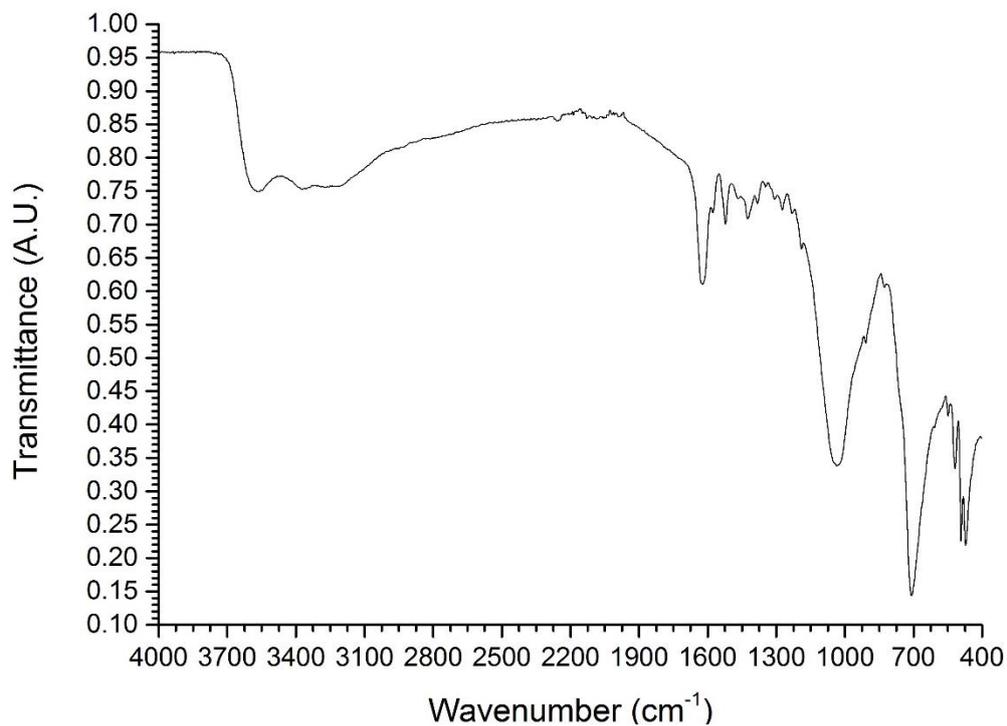
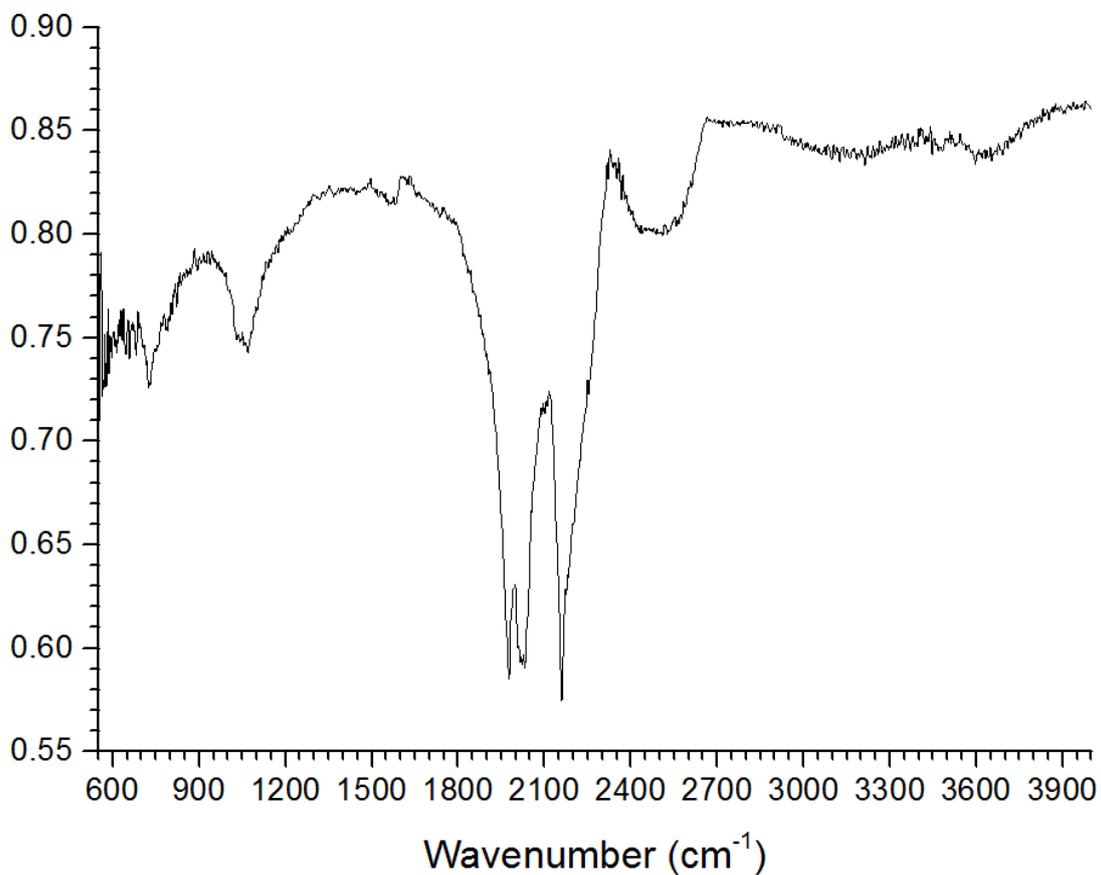


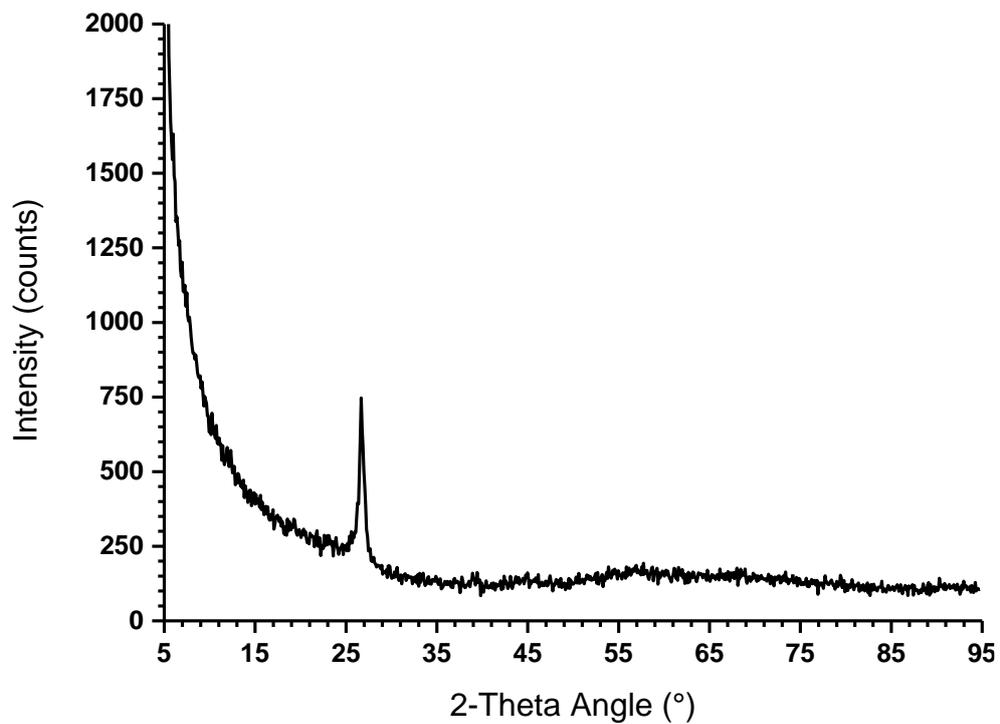
Figure 6. FTIR spectrum of the dye modified graphene



Physisorption experiment.

A solution of MDAP (10 mg) was prepared in EtOH (10 mL) and GnP (7.5 mg) was added. The mixture was stirred for 2 hrs. The sample was then isolated by filtration and washed with Acetone (3x 15 mL) and dried on the filter.

Figure 7. XRD pattern of a mix of DyeH and GnP after 2 hr stirring in EtOH



Raman spectra acquired from different sample positions.

The positions of the peaks were determined by acquiring several Raman spectra from multiple positions of the sample, the base line was subtracted and the positions were determined by Lorentzian fit.¹

Table 1. Corrected D, G, 2D pick positions from multiple points P1-P6 of the mGnP sample

	D-band Value \pm Standard Error	G-band Value \pm Standard Error	2D-band Value \pm Standard Error
Hybrid average	1352.919333	1570.642205	2693.796547
Position 1	1351.40164 \pm 1.10869	1574.62272 \pm 0.29082	2696.16522 \pm 0.78014
Position 2	1344.76863 \pm 2.72565	1566.65535 \pm 0.07924	2690.81334 \pm 0.32022
Position 3	1349	1566.54719 \pm 0.2979	2693.867 \pm 1.31054
Position 4	1355.07253 \pm 1.17376	1573.67159 \pm 0.34101	2696.29856 \pm 0.7915
Position 5	1366.15997 \pm 1.69479	1573.91419 \pm 0.38678	2695.68575 \pm 0.89425
Position 6	1351.11323 \pm 5.10047	1568.44219 \pm 0.28987	2689.94941 \pm 0.90854

Table 2. Corrected D, G, 2D pick positions from multiple points P1-P6 of the untreated GnP sample

	D-band Value \pm Standard Error	G-band Value \pm Standard Error	2D-band Value \pm Standard Error
Hybrid average	1344.2642	1571.2305	2692.5905
Position 1	1342	1564.31926 \pm 0.11379	2687
Position 2	1341.64276 \pm 5.91511	1564.97684 \pm 0.31767	2693
Position 3	1348.15026 \pm 0.6258	1581.31761 \pm 0.26079	2702.94172 \pm 0.58506
Position 4	1348	1582.44585 \pm 0.58316	2698.30476 \pm 1.48619
Position 5	1342	1564.31926 \pm 0.11379	2684.29372 \pm 0.47319
Position 6	1343.7919 \pm 0.56819	1570.00418 \pm 0.1584	2690.00287 \pm 0.43389

¹ (a) A. J. Glover, M. Cai, K. R. Overdeep, D. E. Kranbuehl, H. C. Schniepp, *Macromolecules* 2011, **44**, 9821. (b) A. Ferrari, J. Robertson, *Phys. Rev. B* 2000, **51**, 14095. (c) F. Tai, S Lee, J. Chen, C. Wei, S. Chang, *J. Raman Spectrosc.* **2009**, 40, 1055. (d) J. Robertson, *Mater. Sci. Eng. R* 2002, **37**, 129.