Electronic Supplementary Material (ESI) for Chemical Communications

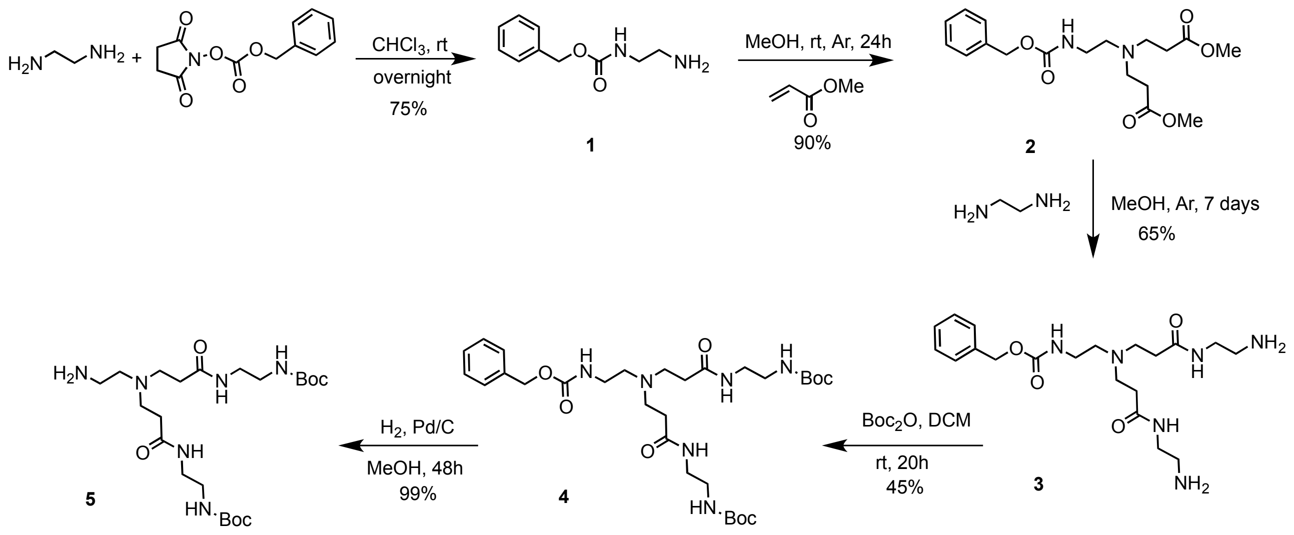
Selective organic functionalization of bulk or graphene edges

Mildred Quintana,*[a] Alejandro Montellano,[a] Antonio Esau del Rio Castillo,[a] Gustaaf Van Tendeloo,[b] Carla Bittencourt[b] and Maurizio Prato*[a]

Electronic Supplementary Information (ESI)

Chemicals. All solvents and chemicals were purchased from Aldrich and used without further purification. Milli-Q water with a resistivity 18.2 MΩ cm was used in Au nanoparticles synthesis. Graphite was purchased from Bay Carbon, Inc. (SP-1 graphite powder, www.baycarbon.com).

Synthesis and characterization of the 1G polyamidoamine Dendron (2)



Synthesis of **1**

Compound **1** was synthesized by a slight modification on the procedure found in literature.[1] A solution of N-(Benzyloxycarbonyloxy)succinimide (3g, 12 mmol) in 20 mL of $CHCl_3$ was added drop by drop via syringe pump in 5h to a solution of ethylendiamine (20 mL, 300 mmol) in 150 mL of $CHCl_3$. After the addition was finished, the crude was magnetically stirred for 8 additional hours. The crude obtained was washed with brine (x3), saturated $NaHCO_3$ (x3) and water (x3). The organic phase was dried with Na_2SO_4, filtered and the solvent removed under pressure obtaining a white solid (1.75g, 75% yield).

Synthesis of **2**

To a solution of **1** (1.75 g, 9mmol) in MeOH (50mL) was bubbled Ar for 15 minutes. Later on, methylacrilate was added drop by drop in excess (2 mL, 22 mmol) leaving it stirring for 24 hours under Ar. The yellow oil obtained was rediluted in $CHCl_3$, washed extensively with brine (x10), dried with Na_2SO_4, filtered, and the solvent removed under reduced pressure obtaining a colorless oil (3g, 90% yield).

^1H NMR (200 MHz, CD_3OD, δ/ppm): 7.38-7.34 (m, 5H, CH_{Ar}); 4.90 (s, 2H, Ar-CH_2); 3.11

(m, 4H, *J*=6 Hz, NH-CH_2-CH2); 2.80 (s, 6H, O-CH_3) 2.63 (m, 8H, *J*=6 Hz, N-CH_2-CH_2-CO)

^{13}C NMR (50 MHz, CD_3OD, δ/ppm): 175.46, 158.78, 138.41, 129.58 (Ar), 129.13 (Ar), 128.99 (Ar), 70.2, 65.60, 52.58, 51.4 (OCH_3), 51.11.

MS (API I Perkin Elmer) ESI m/z : found 367.20 (M+1), calculated 366.18

FT-IR (KBr) ν (cm_{-1}) = 3500, 2910, 2852, 2525, 2335, 1694, 1240, 950, 796, 755, 695.

Synthesis of **3**

A solution of **2** (3g, 8mmol) in 5 mL of MeOH was added via addition funnel to a cooled solution (0ºC) of ethylendiamine (3.5 mL, 50mmol) in MeOH 10mL, and leaved by stirring for 7 days under Ar. The crude of reaction was washed with brine (x5) and saturated $NaHCO_3$ (x5) until remotion of the excess of ethylendiamine. The organic solvent was removed under pressure obtaining a yellow oil (2.3 g, 65% yield) that was used for the next reaction without further purification, while an aliquote was purified by silica gel chromatography for characterization ($CHCl_3$/MeOH 9:1).

^{1}H NMR (200 MHz, CD_3OD, δ/ppm): 7.38-7.34 (m, 5H, CH_{Ar}); 4.90 (s, 2H, Ar-CH_2); 3.11 (m, 6H, *J*=6 Hz, NH-CH_2); 2.63 (m, 8H, *J*=6 Hz, N-CH_2-CH_2-CO and CH_2-NH_2); 2.44 (t, 2H,

J=6 Hz, N-CH_2-CH_2-NH); 2.23 (t, 4H, *J*=6 Hz, CH_2-CO).

^{13}C NMR (500 MHz, CD_3OD, δ/ppm): 175.46, 158.78, 138.41, 129.58 (Ar), 129.13 (Ar), 128.99 (Ar), 67.60, 53.78, 51.11, 42.41, 41.97, 39.91, 34.82.

MS (API I Perkin Elmer) ESI m/z: found 423.3 (M+1), 445.3 (M+Na); calculated 422.522

FT-IR (KBr) ν (cm^{-1}) = 3419, 2954, 2926, 2852, 2525, 2238, 2075,1694, 1635, 1553, 1456, 1265, 1117, 973, 775, 745, 700.

Synthesis of **4**

To a cooled solution (0ºC) of **3** (100mg, 0.25 mmol) in $CHCl_3$ (5mL) was added drop by drop via addition funnel a solution of Boc_2O in DCM (5mL) and leaved under vigorous magnetic stirring for 2 days. The organic solvent was removed under pressure obtaining a mixture of non-Boc protected, mono and bis-protected derivative. This mixture was purified by silica gel chromatography ($CHCl_3$ 95 MeOH 5) obtaining 4 as a white oil (70 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.35-7.31 (m, 5H, CHAr); 7.13 (bs, 2H, CH_2-CO-NH); 5.82 (bs, 1H, Cbz-NH); 5.31 (bs, 2H, NH-Boc); 5.07 (s, 2H, Ar-CH_2); 3.34-3.06 (m, 10H, NH-CH_2);

2.66 (t, 4H, CH_2-N-$(CH_2)_2$); 2.49 (t, 2H, CH_2-N-(CH_2)2); 2.28 (t, 4H, CH_2-CO); 1.41 (s, 18H, NH-Boc).

^{13}C NMR (500 MHz, CDCl3, δ/ppm): 172.87, 156.41, 136.48, 128.43 (Ar), 128.13 (Ar), 128.09 (Ar), 79.34, 66.57, 52.67, 50.07, 40.30, 39.77, 38.74, 34.08, 28.40

MS ESI m/z : found 623.4 (M+1), 645.3 (M+Na); calculated 622.753

FT-IR (KBr) ν (cm^{-1}) = 3327, 3068, 3036, 2976, 2934, 2849, 2828, 1695, 1653, 1539, 1438, 1392, 1366, 1339, 1272, 1253, 1170, 1039, 1027, 1011, 862, 778, 754, 737, 698, 460.

Synthesis of **5**

To a solution of **4** (70 mg, 0.112 mmol) in MeOH previously degassed for 10 minutes by bubbling N_2 was added a catalytic amount of Pd/C (10% w/w). The reaction was leaved for 24 hours under H_2 atmosphere to finally filtered it in celite and removed the solvent under reduced pressure, obtaining a white sticky solid in quantitative yield (55 mg)

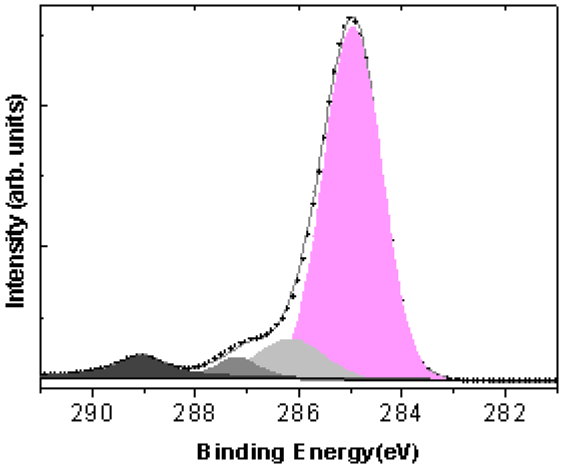
^{1}H NMR (500 MHz, CD_3OD, δ/ppm): 3.23 (m, 4H, CH_2-NH); 3.16 (m, 4H, CH_2-NHBoc); 2.99 (m, 2H, CH_2-NH_2); 2.72 (m, 6H, CH_2-N); 2.36 (t, 4H, *J*= 5 Hz, CH_2-CO); 1.44 (s, 18H, NH-Boc).

^{13}C NMR (500 MHz, CD_3OD, δ/ppm): 175.12, 148.42, 80.12, 52.65, 51.13, 43.91, 40.88, 40.59, 38.80, 34.26, 34.04, 30.78, 28.78, 20.17

MS (API I Perkin Elmer) ESI m/z : found 489.4 (M+1); calculated 488.621

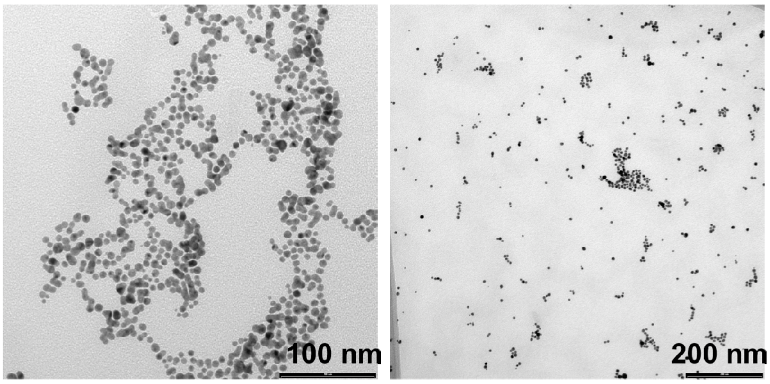
FT-IR (KBr) ν (cm^{-1}) = 3302, 3072, 2977, 2931, 2872, 2852, 1703, 1694, 1657, 1651, 1538, 1455, 1392, 1366, 1275, 1252, 1171, 1040, 1027, 1013, 861, 781, 757, 590, 465.

Characterization techniques. TEM measurements were performed on a TEM Philips EM208, using an accelerating voltage of 100 kV. Samples were prepared by drop casting from the dispersion onto a TEM grid (200 mesh, Nickel, carbon only). X-ray photoelectron spectroscopy (XPS) measurements were performed in a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a Monochromatic Al Kα X-Ray (hν=1486.6 eV) source with a highly focused beam size that can be set from 10μm to 300 μm. The beam size used was 100 μm. The energy resolution was 0.6 eV. For the compensation of the built up charge on the sample surface during the measurements, dual beam charge neutralization composed of an electron gun (~1eV) and the Argon Ion gun (≤10eV) was used. For the XPS analysis the samples were drop cast on conventional TEM grids (200 mesh, copper) and left to dry. The total covering of the grids 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. 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. Raman spectra were recorded with an Invia Renishaw microspectrometer (100x) equipped with laser at 532 nm. Samples were recorded from drops of the dispersions of graphene products in DMF deposited on glass surfaces. Surfaces were left to dry at room temperature. For the AFM analysis, 100μl of each sample with a concentration of 2 μgml^{-1} were spin coated (4000 RPM, 6 min) over fresh cleaved mica, gently rinsed with water, and blown with dry nitrogen, finally the samples were dry under vacuum in order to remove the excess of solvents. The samples were characterized using a Nanoscope V (Digital Instruments Metrology Group, model MMAFMLN) in tapping mode in air at room temperature, using standard μmash® SPM probe (NSC15/AIBS) with tip height 20-25μm, cone angle <40° (Resonant frequency 325kHz, force constant of ~46N/m). Image analysis was performed with WsXM software (Nanotec Electronica S. L.).[2]

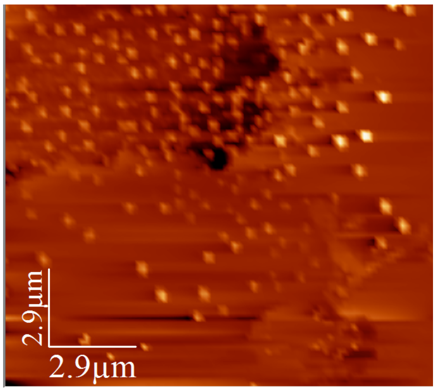


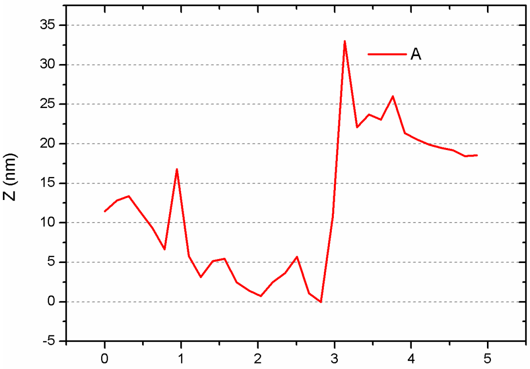
SI-1. Photoemission spectra and fit of the C 1s core level region of **4**.

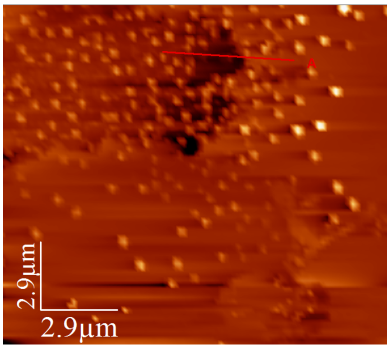
Au nanoparticles synthesis. The pH of deoxygenated water-methanol solution (1M) of chloroauric acid (2 mM) was adjusted to 5 by the addition of citric acid (1.5 M). Then, the mixture was irradiated with UV light (GE.R 500W Helios Italquartz – 250-450 nm, λ_{max}=360 nm) for an interval of 60 min under magnetic stirring. The size distribution of the resulting nanoparticles (calculated from 110 nanoparticles) is found to be 6.2 ± 1.2 nm. TEM images are shown in SI-3.

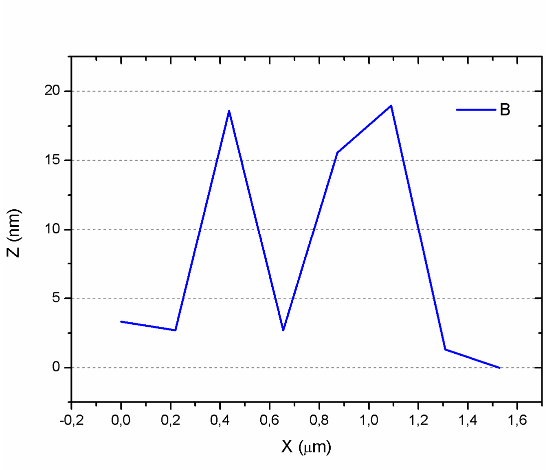


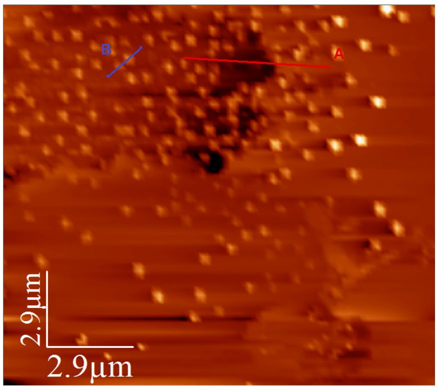
SI-3. TEM images of Au NPs growth under UV-light irradiation.



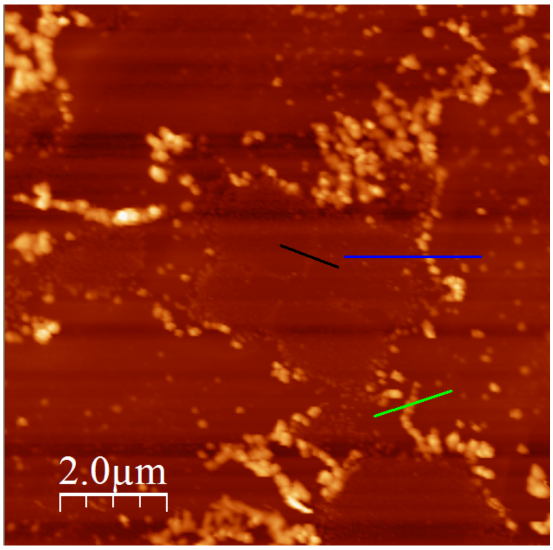


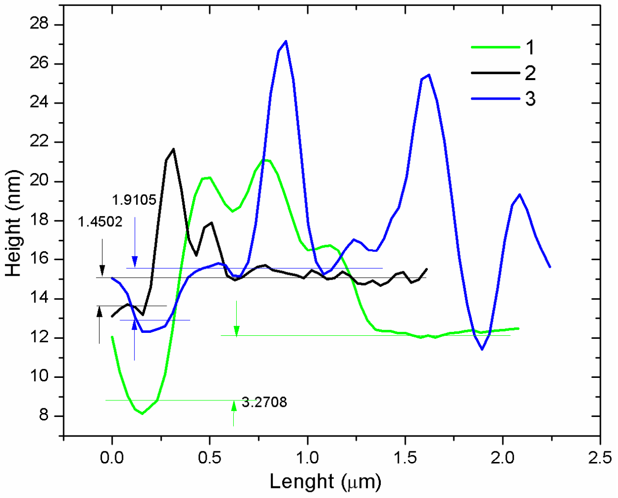


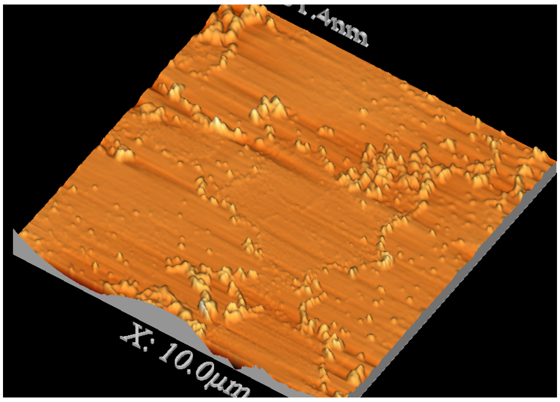




SI-4. AFM analysis of **3**







SI-4. AFM analysis of **4**

---

[1] Otoda, K.; Kimura S.; and Y. Imanishi. *Bull. Chem. Soc. Jpn.* 1990, 63, 489.

[2] Horcas, R.; Fernandez, J.M.; Gomez-Rodriguez,; J. Colchero,; J. Gomez-Herrero and A. M. Baro, *Rev. Sci. Instrum*. 2007, 78, 013705.