Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Deterministic Organic Functionalization of Monolayer Graphene Via High Resolution Surface Engineering

Electronic Supporting Information

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AFM images of patterned graphene

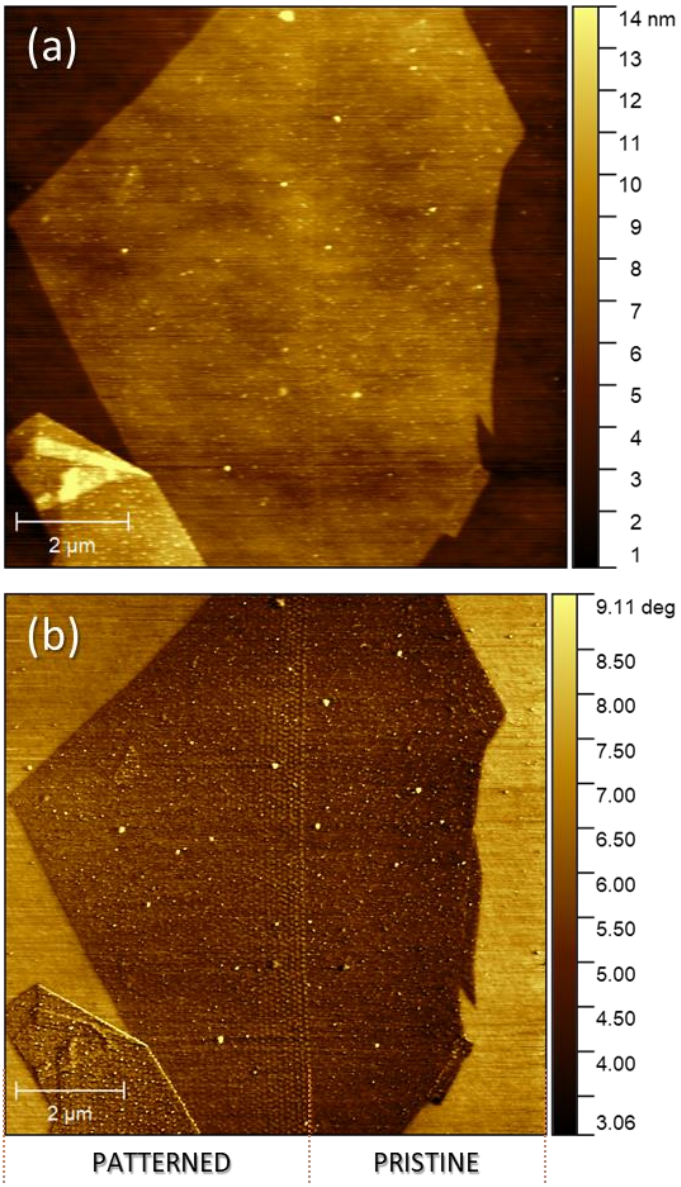

Figure S1. AFM (a) height and (b) phase images (10x10 µm^2) of Flake 1. As indicated below the figure, the left side of the flake is patterned, the right side is pristine.

1,3-DC of azomethine ylide

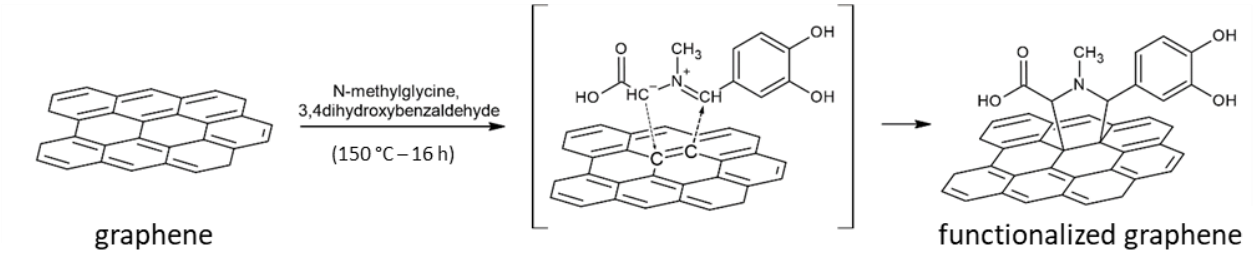

Figure S2. Schematic representation of the in-situ 1,3-DC of azomethine ylide on graphene.

The reaction mechanism of the 1,3-DC is well known.[1] In order to optimize the reaction, the use of the N-methylated α-amino acid is crucial. In fact, the condensation of a secondary amine with an aldehyde forms a positive charged imine. The presence of an electron-withdrawing group, like the carboxylic group, on the alpha carbon easily leads to the deprotonation and the formation of the azomethine ylide. Moreover, the presence of the aromatic ring of the aldehyde can favor the alignment of the ylide with the graphene lattice, thanks to π- π interactions. According to the Sustman's terminology, in the case of a 1,3-dipolar cycloaddition reaction of an azomethine ylide, the dominant interaction (using the *frontier molecular orbitals theory*) is that of the $HOMO_{azomethine\ ylide}$ with the $LUMO_{graphene}$.[2] In previous work,[3] sodium carbonate was added in order to prevent the loss of the carboxyl group of the azomethine ylide. Here, the functionalization procedure was initially performed with and without the adding of the sodium carbonate, with no evidences of changes in the Raman analysis of the functionalized graphene. After the 1,3-dipolar cycloaddition, the carboxyl group would be partially lost, due to the temperature of the reaction environment. Anyway, in order to minimize the number of reagents, simplifying the reaction and avoiding undesirable residues (which would appear in any further chemical analysis such as the XPS, as shown in a previous work),[3] and considering that the Raman analysis of the functionalized graphene shows the vibrational peak arising from the carboxyl group (confirming its presence in the final product) the functionalized procedure is performed without the addition of sodium carbonate. In fact, it is known[4] that the sarcosine does not undergo decarboxylation before closing the 1,3-dipolar cycloaddition, hence the effectiveness of the functionalization is not affected.

Raman Analysis

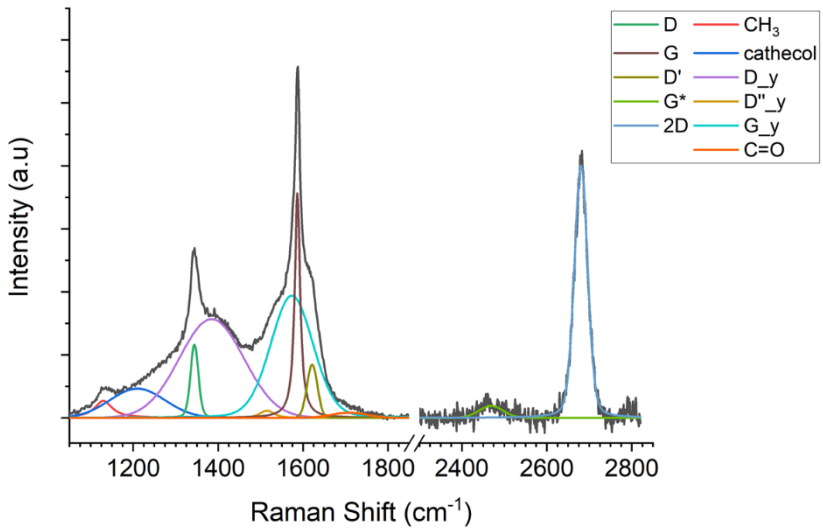

Figure S3. Raman spectrum of the functionalized Flake 2 collected at 5% laser power (the parts of the spectrum before and after the break were collected in different measurements, shown in Fig. S5). A fit to the data is also shown.

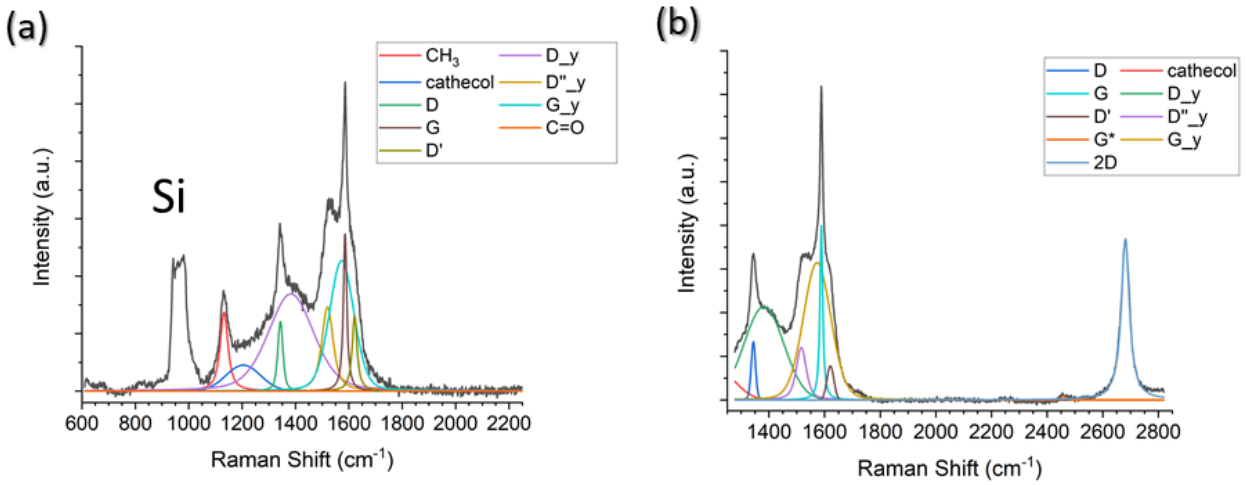

Figure S4. Complete Raman spectra of the (a) lower and (b) higher Raman shift region, collected on functionalized patterned graphene (Flake 3) at 0.5% laser power. The fit for each spectrum is shown. The broad band [920 – 1050] cm^{-1} originating from the Si signal of the silica substrate is visible in panel (a).

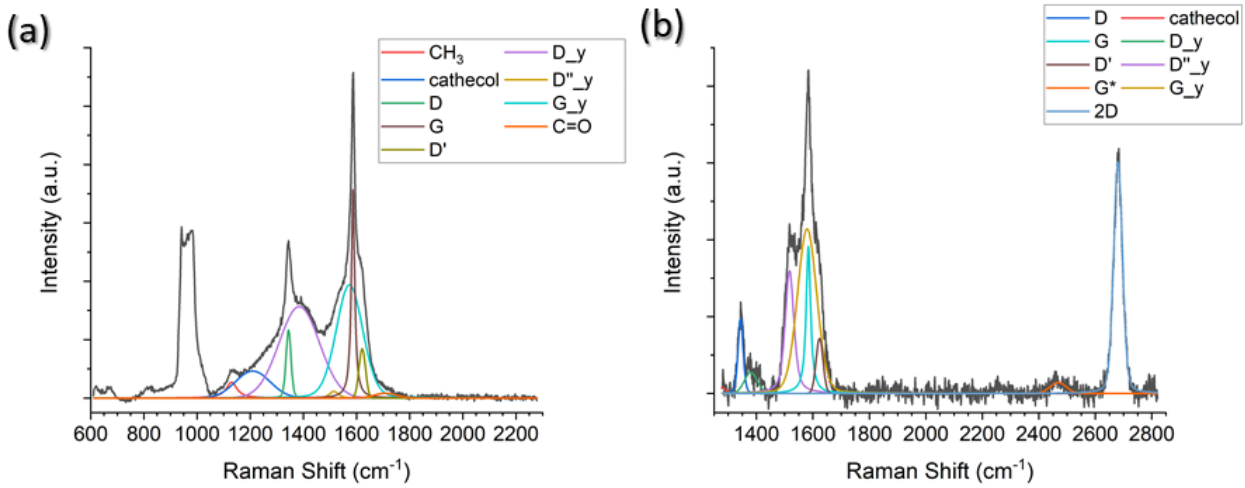

Figure S5. Complete Raman spectra of the (a) lower and (b) higher Raman shift region, collected on functionalized patterned graphene (Flake 2) at 5% laser power. The fit for each spectrum is shown. The broad band [920 – 1050] cm^{-1} coming from the Si signal of the silica substrate is visible in panel (a).

Computational Simulation

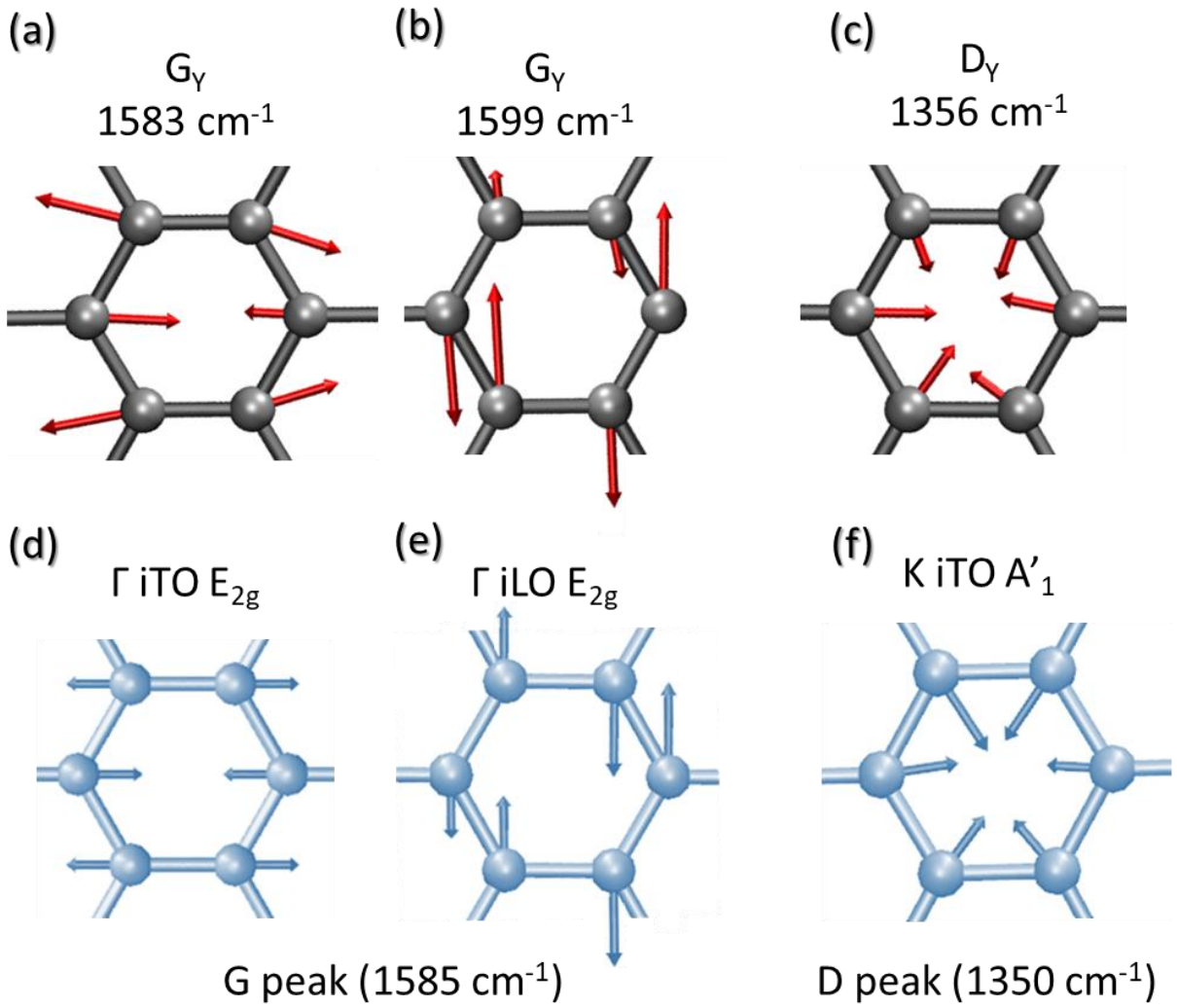

Figure S6. Computed vibrational normal modes (calculated using the VIBRATIONAL-ANALYSIS module of CP2K) in the region of (a-b) the G_Y and (c) the D_Y band, slightly different from the well-known classic normal modes of (d-e) the G peak in pristine graphene and (f) the D peak in defective graphene.[5]

AFM images of functionalized patterned graphene

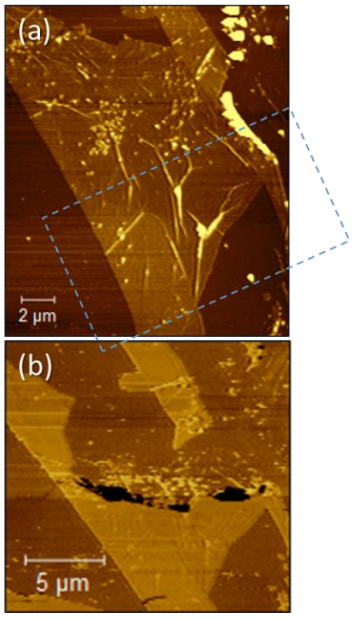

Figure S7. (a) AFM height image of Flake 3 after low-energy EBI (the blue rectangle shows the area which was exposed). (b) AFM phase image of Flake 3 after functionalization: the most part of the non-irradiated area detaches and folds. Here, also part of the patterned area has folded.

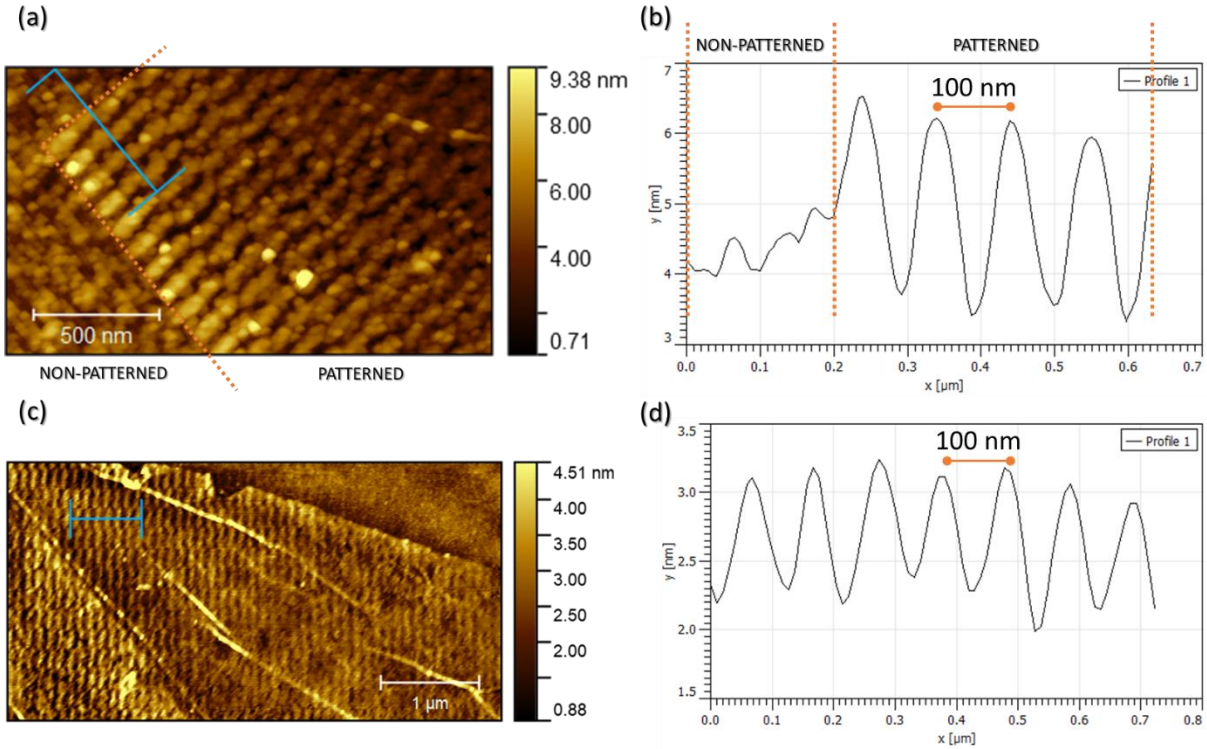

Figure S8. (a) AFM height image of Flake 2 after the functionalization showing both a patterned area (on the right) and a non-patterned area (on the left) as indicated. (b) Profile taken along the blue line in panel (a) showing a step size of 100 nm, as originally designed via EBI, only in the patterned area. (c) AFM height image of the patterned area of Flake 2 after the functionalization. (d) Profile taken along the blue line in panel (c), showing a step size of 100 nm, as originally designed via EBI.

Computational Simulation - supercell

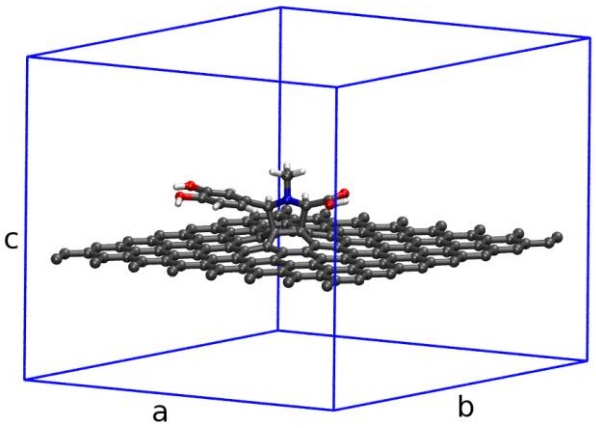

Figure S9. Hexagonal graphene supercell (a = b = 1.98 nm, c = 2 nm) consisting of 154 atoms (128 graphene's carbons plus 26 atoms of the ylide molecule).

REFERENCES

[1] J. H. Ryan, 1,3-Dipolar cycloaddition reactions of azomethine ylides with aromatic dipolarophiles, *ARKIVOC: Online Journal of Organic Chemistry*, **2015**, 160-183.

[2] K. V. Guthelf et al., *Chemical Reviews*, **1998**, 98, 863−909.

[3] L. Basta et al., Covalent organic functionalization of graphene nanosheets and reduced graphene oxide via 1,3-dipolar cycloaddition of azomethine ylide, *Nanoscale Advances*, **2021**, 3, 5841-5852.

[4] E. M. Martinis et al*., European Journal of Organic Chemistry*, **2021**, 3545–3551.

[5] A. Jorio et al., Vibrations in graphene, *2D Materials*, **2017**, 71-89.