

Supporting Information

Multicomponent Covalent Chemical Patterning of Graphene

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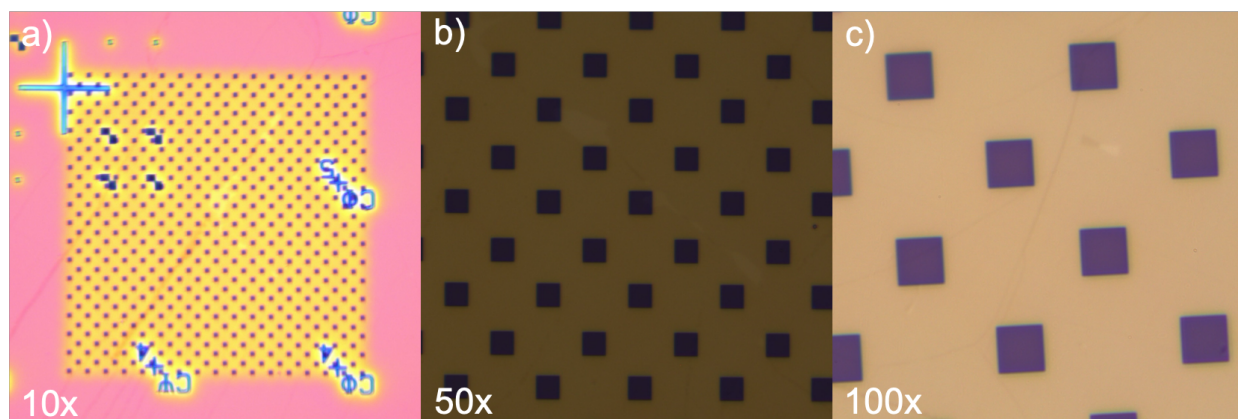


Fig S1. Optical images of the patterned SLG/SiO₂ at different magnifications. Single squares have a dimension of 5 μm x 5 μm .

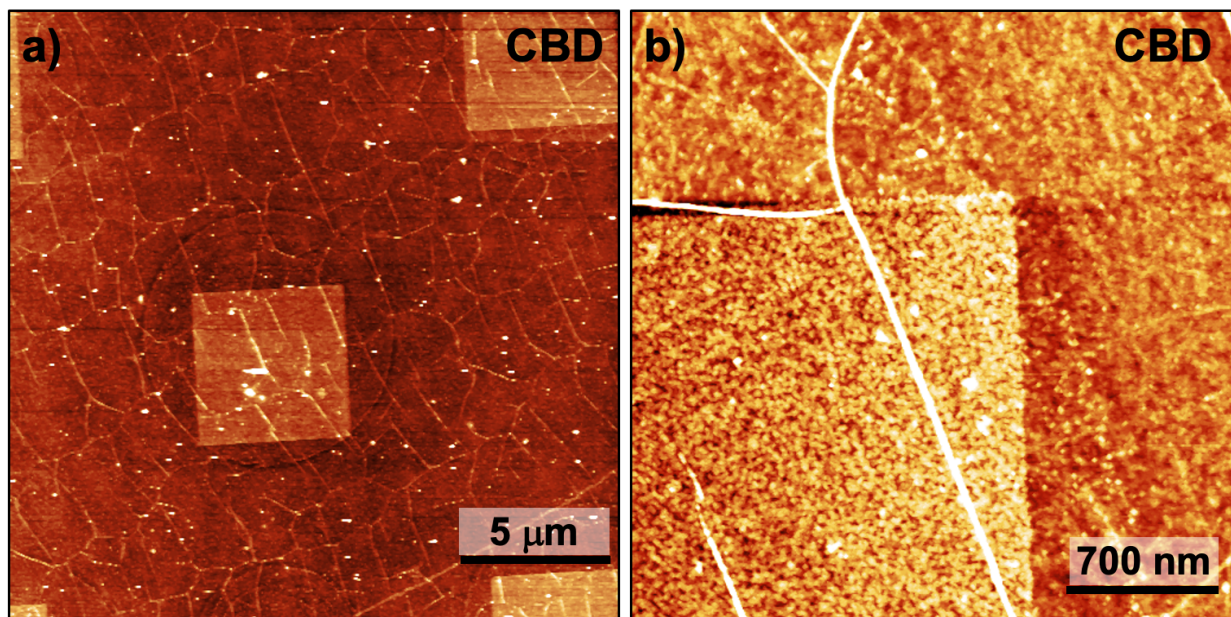


Fig S2. (a) A representative small scale AFM image showing the nanostructured and granular morphology of the chemical pattern (CBD).

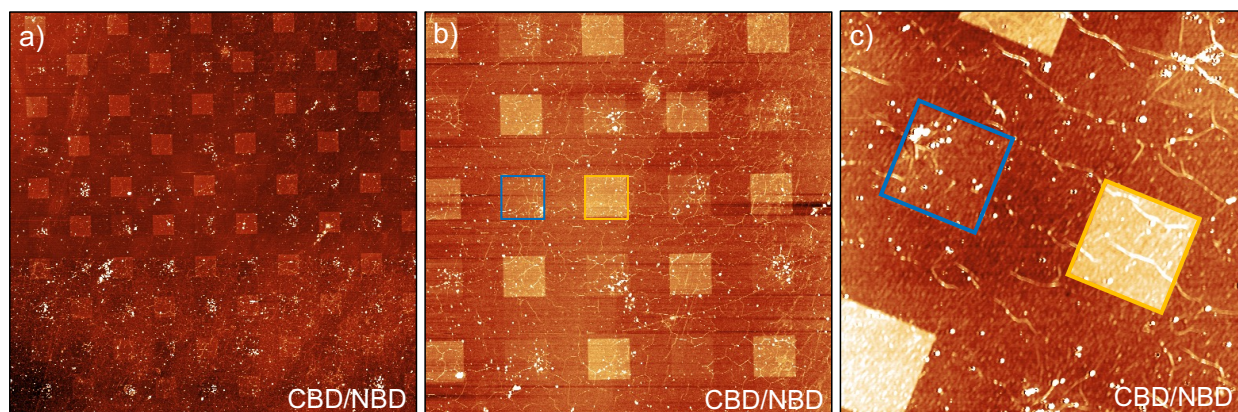


Fig S3. Additional AFM topography images of the SLG/SiO₂ covalently patterned using CBD and NBD. The brighter and thus the thicker squares correspond to the chemical pattern formed by CBD. (a) 100 $\mu\text{m} \times 100 \mu\text{m}$ and (b) 50 $\mu\text{m} \times 50 \mu\text{m}$. (c) 22 $\mu\text{m} \times 22 \mu\text{m}$.

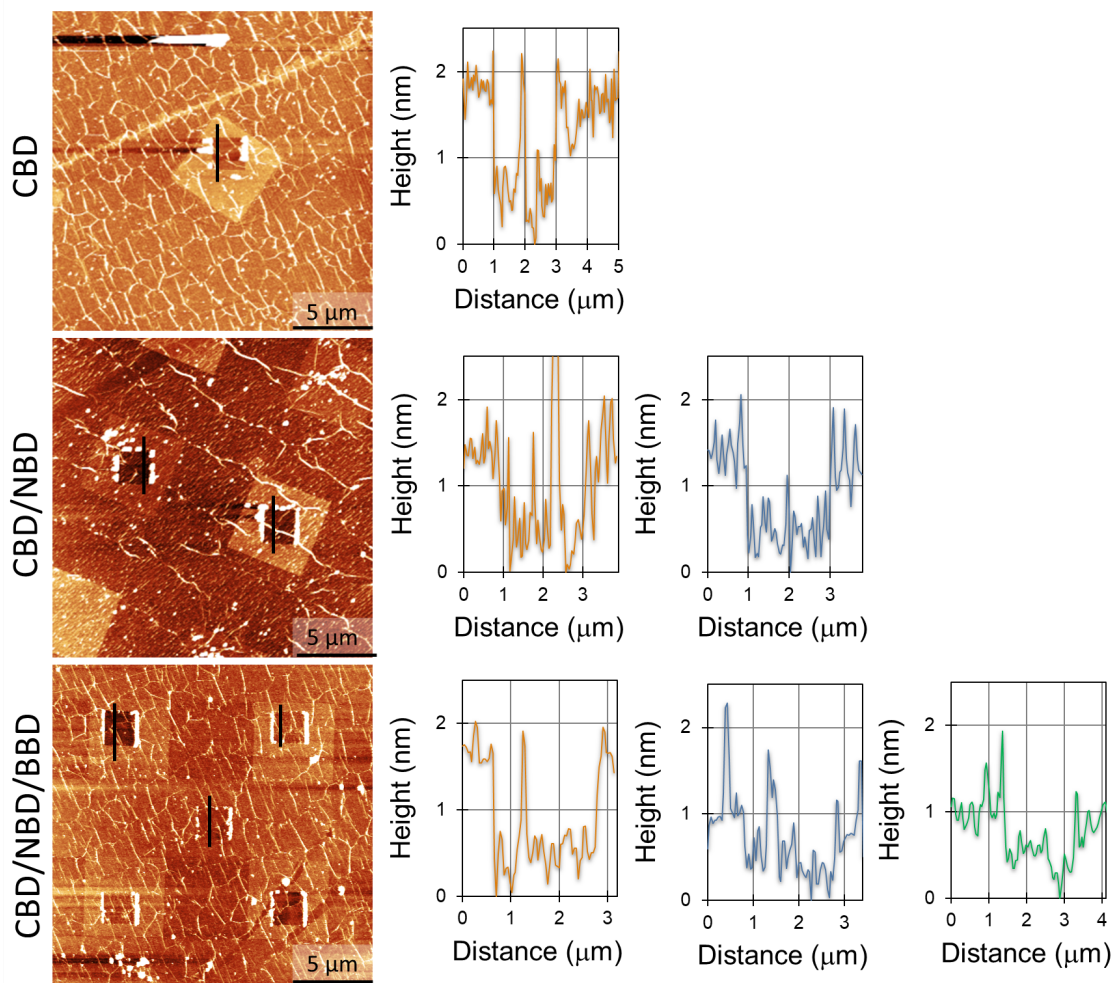


Fig S4. AFM topography data showing how the layer thickness of each pattern was obtained. Contact-mode AFM was used to locally remove the covalent pattern at a constant vertical tip force. All cantilever spring constants (nN/nm) were calibrated before each experiment applying a thermal single harmonic oscillator model. Force curves allowed extraction of the deflection optical lever sensitivity (nm/V) from the slope of repulsive part in the force curve. Both parameters combined allow to determine the setpoint (V) required for a given force. The AFM images in the figure show representative scratched squares highlighting a clean, flat graphene pit surrounded by a rough, high edge that is formed as a result of the accumulation of the material removed from grafted film. The film thickness was then calculated by fitting gaussian curves through the peaks present in the height histogram of the topographic image and obtaining the difference between the two peaks.

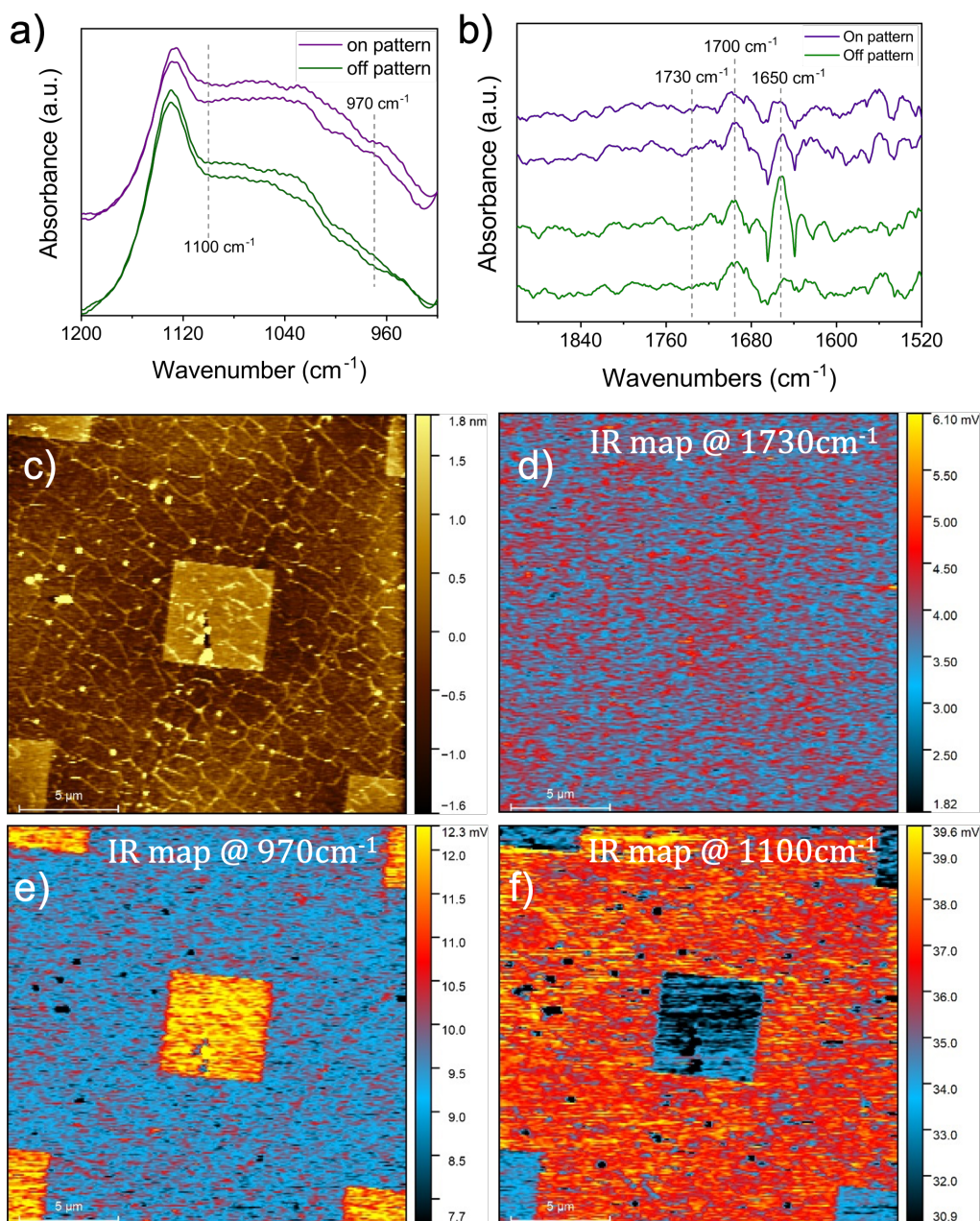


Fig S5. (a, b) Representative IR spectra obtained on- and off- the chemical patterns using AFM-IR in different range of wavenumbers for SLG patterned using CBD. (c) AFM topography image of the surface prior to IR mapping. (d) AFM-IR map at 1730 cm^{-1} . (e) AFM-IR map at 970 cm^{-1} . (f) AFM-IR map at 1100 cm^{-1} . Note that at 1100 cm^{-1} the patterned squares show a lower amplitude against the surface.

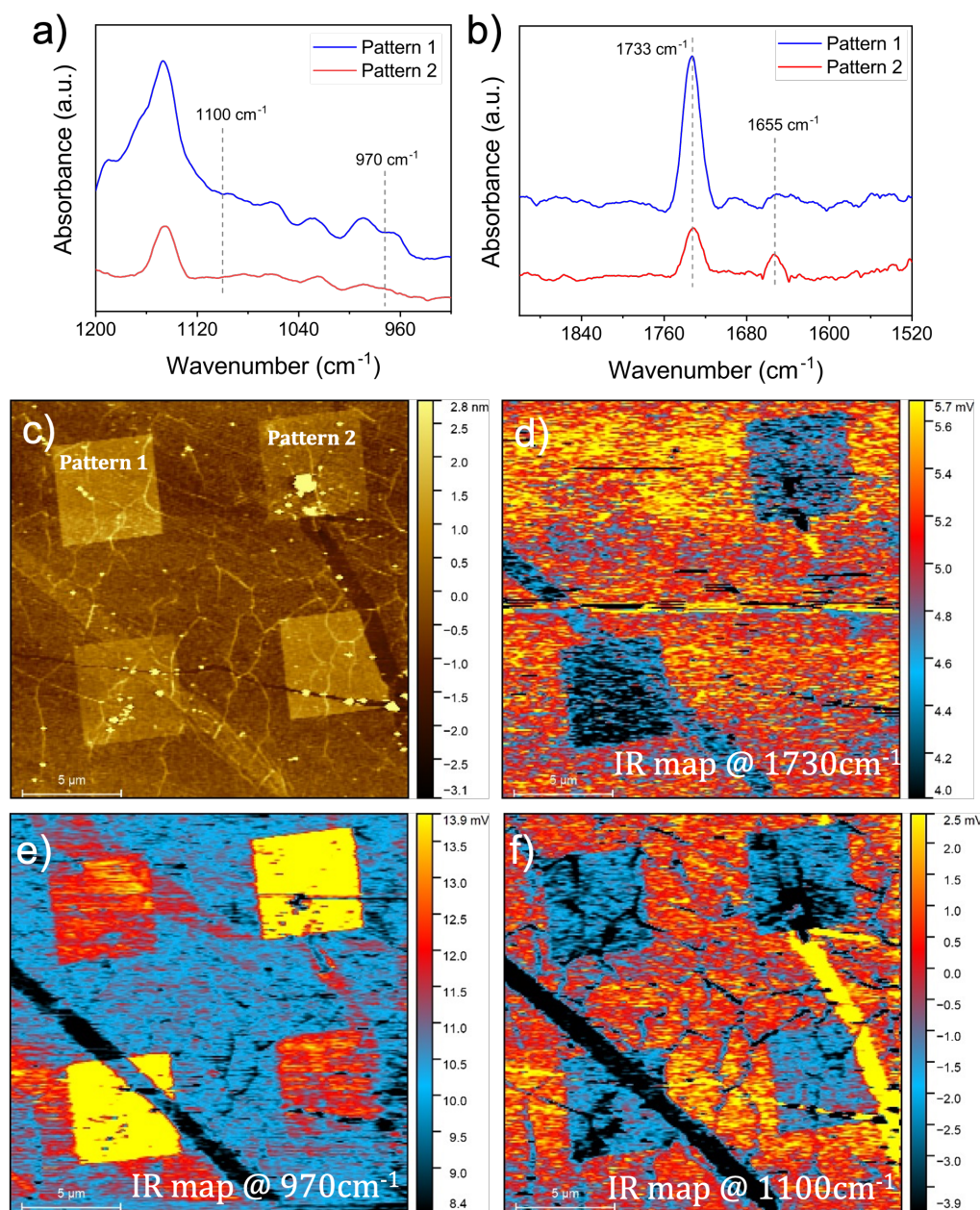


Fig S6. (a, b) Representative IR spectra obtained on the two different chemical patterns using AFM-IR in different range of wavenumbers for SLG patterned using CBD and NBD. (c) AFM topography image of the surface prior to IR mapping. (d) AFM-IR map at 1730 cm^{-1} . Note that two squares show a poorer contrast against the rest of the surface at this wavenumber indicating the absence of carbonyl groups. These are the nitrophenyl squares. (e) AFM-IR map at 970 cm^{-1} . The two types of patterned squares show dissimilar contrast indicating the presence of chemically distinct functionalities. (f) AFM-IR map at 1100 cm^{-1} . Note that at 1100 cm^{-1} the patterned squares show a lower contrast against the surface.

XPS analysis of the covalently patterned surfaces

The formation of only a monolayer of grafted units on the surface and the unavoidable presence of polymeric residues from the lithography step make complicated to extract quantitative information about the chemical composition on the surface by using XPS. The survey spectra of the four samples were analyzed with respect to changes in the carbon, nitrogen and bromine content relative to silicon from the support material and relative to bare graphene on the support material (Table S1 and Fig S7 (left)). The changes in carbon content are negligible and do not support conclusions regarding the grafting of species onto the graphene support. This is corroborated by the carbon 1s high resolution spectra which show minimal changes between all four samples tested (Fig. S7, right).

Table S1. Atomic ratios ($\times 1000$) for each of the samples, derived from the survey spectra

Sample	C/Si	N/Si	Br/Si
Reference	2.12	14	0
CBD	1.94	16	0
CBD NBD	2.30	53	0
CBD NBD BBD	1.93	18	4.31

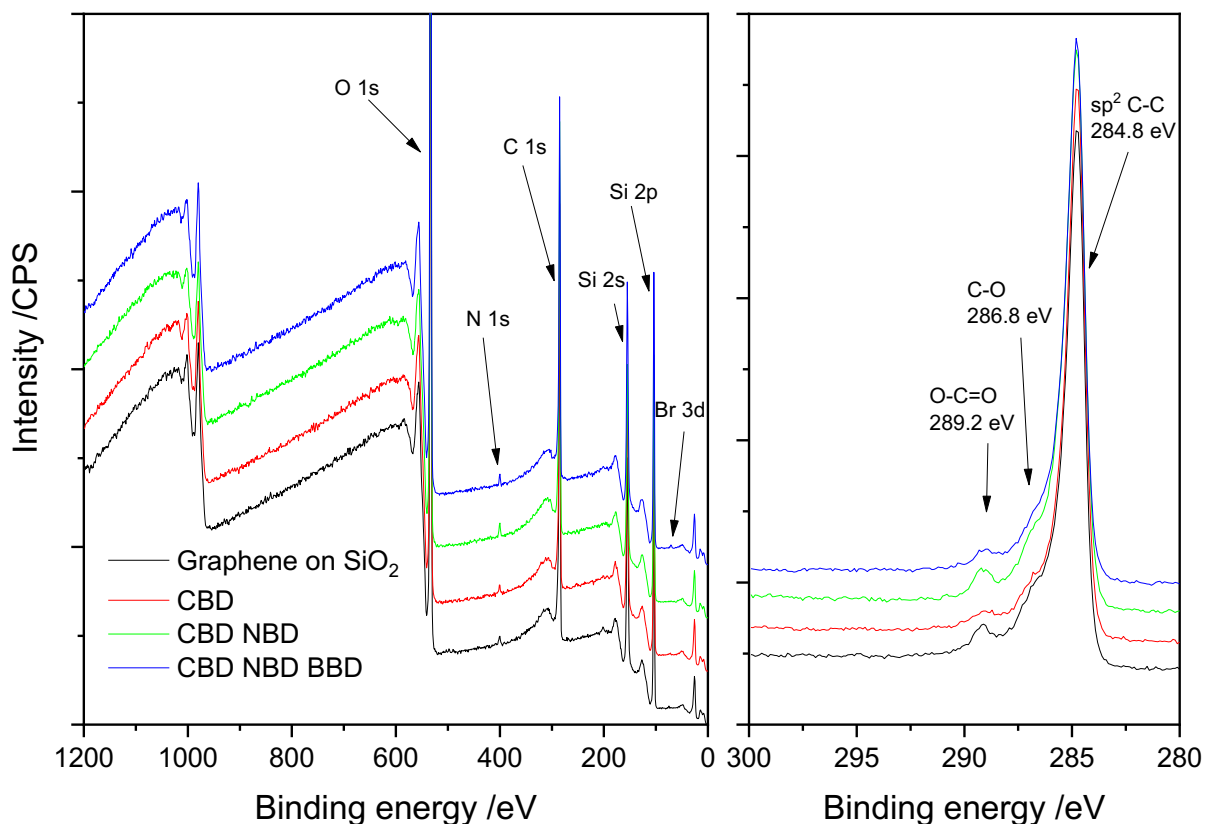


Fig S7. XPS survey spectra (left) and carbon 1s spectra (right) of pristine graphene on SiO₂, CBD, CBD, NBD and CBD, NBD, BBD modified graphene on SiO₂.

The most important conclusion about the N region high-resolution spectra is the impossibility of determining the presence of nitro groups on the surface. Indeed, looking at the high-resolution nitrogen 1s spectra (**Fig. S8**), there is a complete absence of peaks due to nitro groups which would be expected at approximately 406 eV, with the only detected peak for all samples being at approximately 400 eV, which could correspond with amines or amides.¹

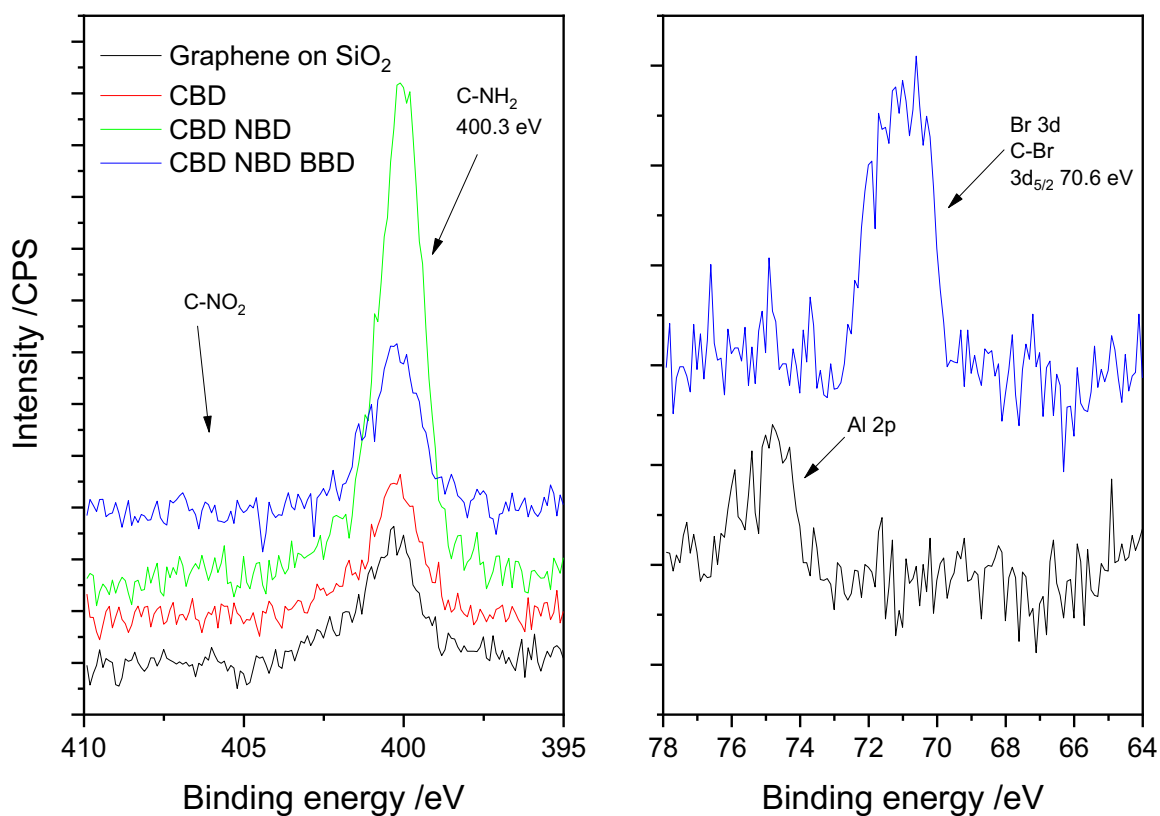
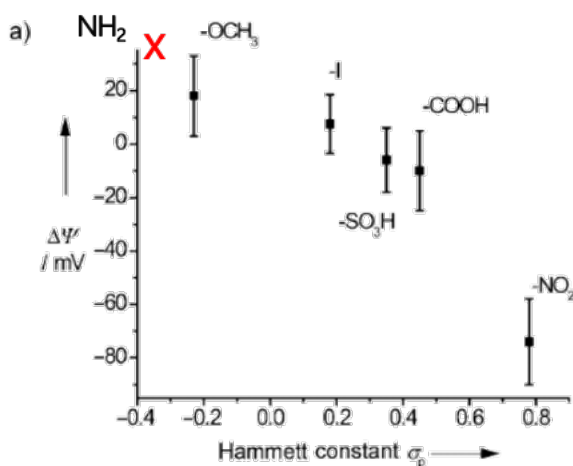


Fig. S8. Nitrogen 1s spectra (left) and bromine 3d spectra (right) of the modified graphene samples. Finally, a low level of bromine was observed in the BBD containing sample, which a high resolution bromine 3d spectrum confirms is due to C-Br (Br 3d_{5/2} at 70.6 eV).²

KPFM discussion:

Stark *et al.* provided a correlation between the Hammett constant and the changes measured in the surface potential upon covalent binding of different aryl groups to the basal plane of graphite.³ Their study showed a qualitative correlation between the changes in the surface potential and the Hammett constant. The plot provided below shows the correlation observed by Stark and co-workers. Note that the surface potential for $-\text{NO}_2$ grafted HOPG in their case is lower than that of $-\text{COOH}$ groups. In the case of covalently patterned graphene however, the CPD of nitrophenyl modified areas was found to be higher than that of carboxyphenyl modified areas indicating (partial) reduction of the $-\text{NO}_2$ groups to $-\text{NH}_2$ groups. Based on the Hammett constant of the $-\text{NH}_2$ groups substituted in the para position, one expects a higher value of surface potential (red cross), as observed in the present case. This hypothesis is further corroborated by XPS as well as AFM-IR measurements which confirm the presence of reduced nitrogen species on the surface. We note that the possibility of the reduction of the nitro groups in basic media using ascorbic acid as the reducing agent has been demonstrated in the recent past.⁴



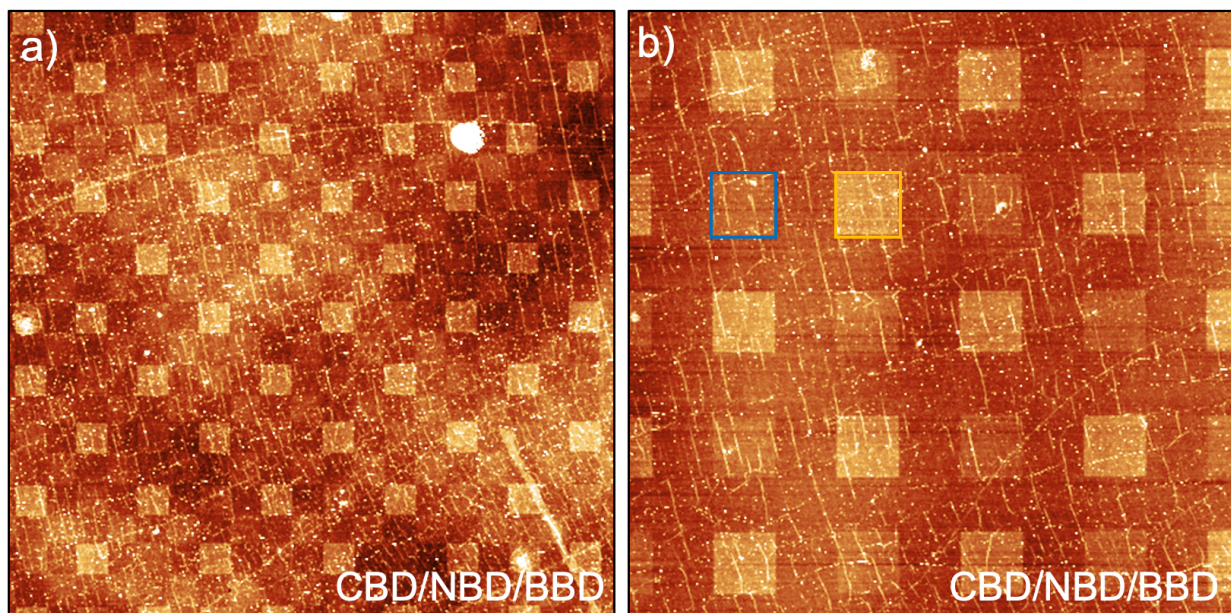


Fig S9. Additional AFM topography images of the SLG/SiO₂ covalently patterned using CBD, NBD and BBD. (a) 100 μm × 100 μm and (b) 50 μm × 50 μm. The square highlighted in blue and yellow indicate the nitrophenyl and the carboxyphenyl patterns, respectively. The area in between these squares is filled with the covalently bound bromophenyl groups.

References:

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