Supplementary Information

Selective self-assembly and light emission tuning of layered hybrid perovskites on patterned graphene

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Videos of the crystallization process

Accelerated videos (5x real speed) of the **Fu** perovskite crystallization observed using optical microscope. The sample was prepared as usual but instead of being annealed on hotplate it was put directly on the microscope stage for observation. It is possible to see how the square shaped seeds slowly induce the crystallization of the whole film. Videos are available to download from the publisher's website.

XRD

After tests to check if the procedure for selective growth on graphene was transferable also to the 3D perovskite (see section "3D perovskite on graphene") XRD were measured to confirm the formation of the desired structure in the sample obtained.

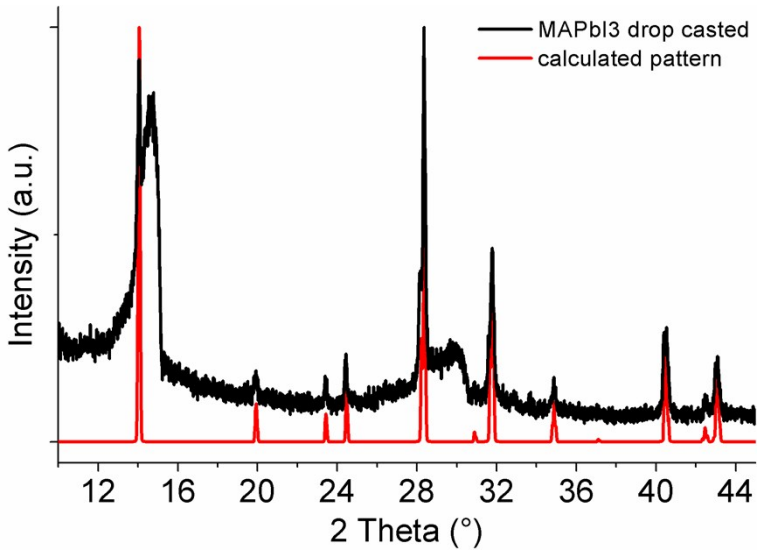

Figure S1. XRD pattern of the 3D perovskite (methylammonium iodide/PbI_2) obtained by drop casting (black line) and calculated pattern from literature (red line). The observed reflections match perfectly with the calculated ones. Broad signals are coming from the substrate (Si/SiO_2)

Raman spectroscopy

Raman spectrum of graphene on a substrate (Si/SiO_2)

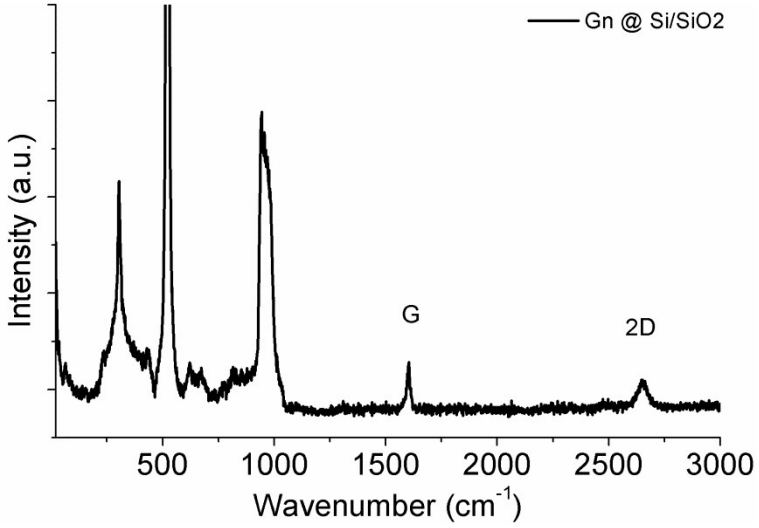

Figure S2. Raman spectrum of graphene on Si/SiO_2 substrate using 633 nm excitation laser under ambient conditions. The intense peaks in the region 250-1000 cm^{-1} are from the Si/SiO_2 substrate while the characteristic graphene modes appear at between 1585-1600 cm^{-1} (G mode) and 2650 cm^{-1} (2D mode). The same spectrum was recorded for each sample to verify the quality of the material before proceeding with the perovskite growth.

Raman fitting

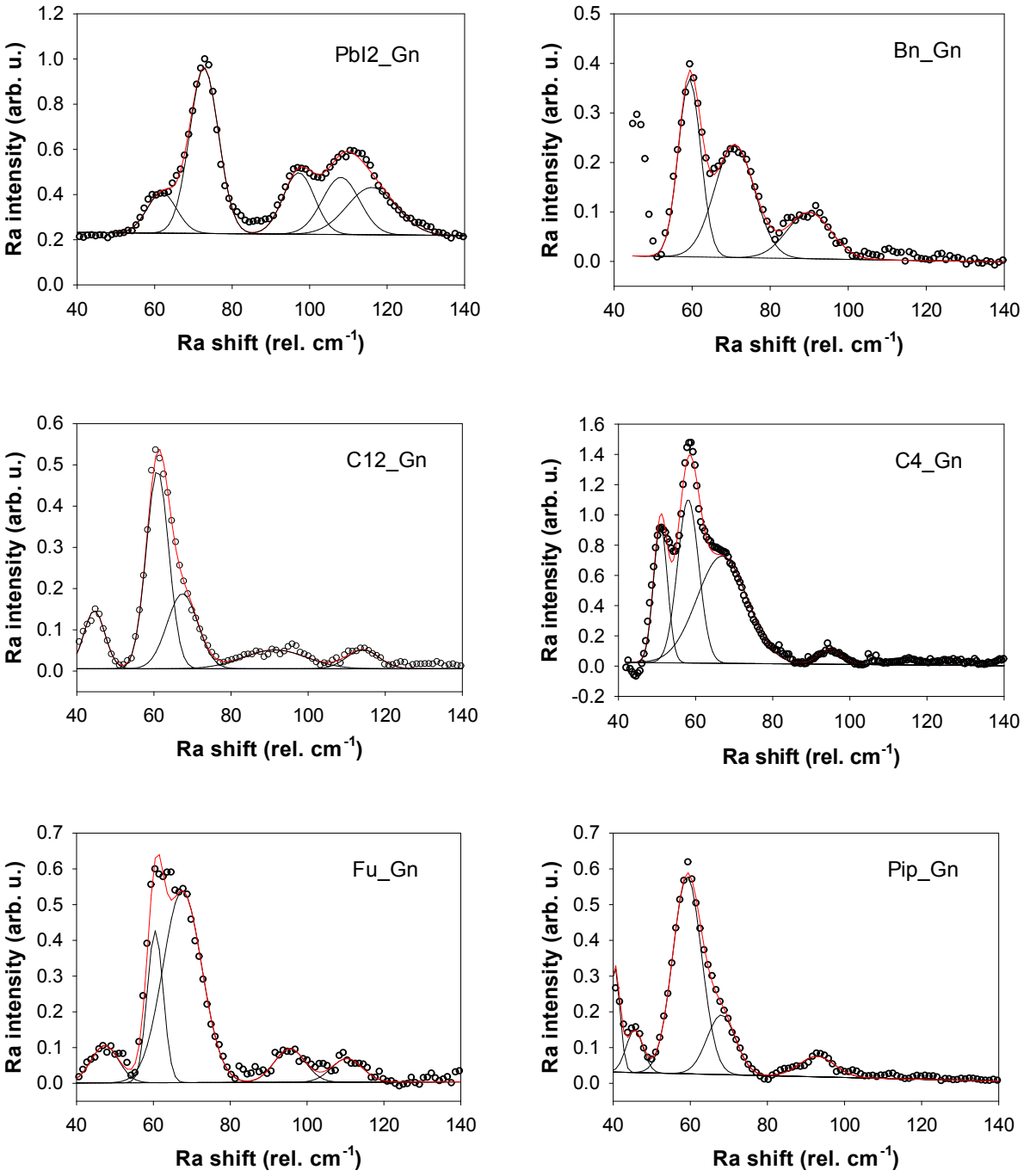

Figure S3. Low-wavenumber region of the Raman spectra of the perovskite (C4, C12, Fu, Pip) and PbI_2 films on graphene (open symbols) together with the total fit corresponding to the Raman bands (red line). The fits of the individual components are shown for each peak (black lines); the peaks with extremely low intensity are not included.

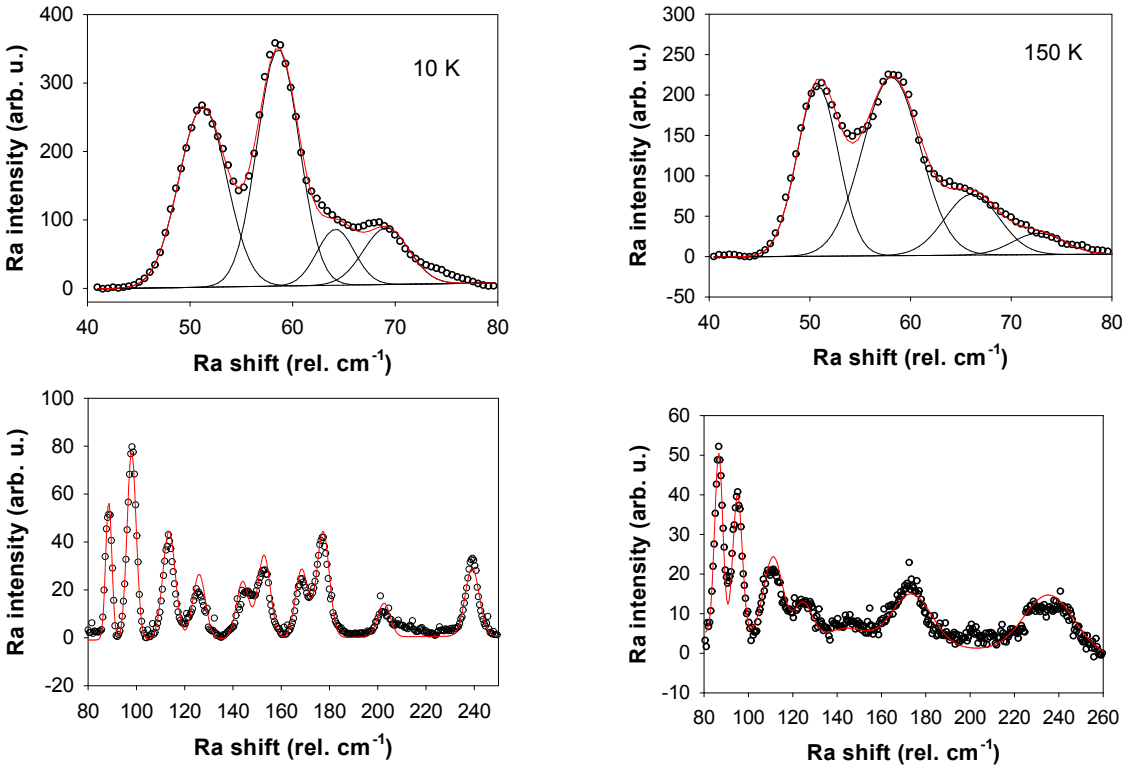

Figure S4. Raman spectra of the C4 perovskite (open symbols) recorded at 10 K and 150 K together with the total fit corresponding to the superposition of the detected Raman bands (red line). The low-wavenumber region is expanded and decomposition of the four components is shown (black line).

AFM of the Pip large area egde

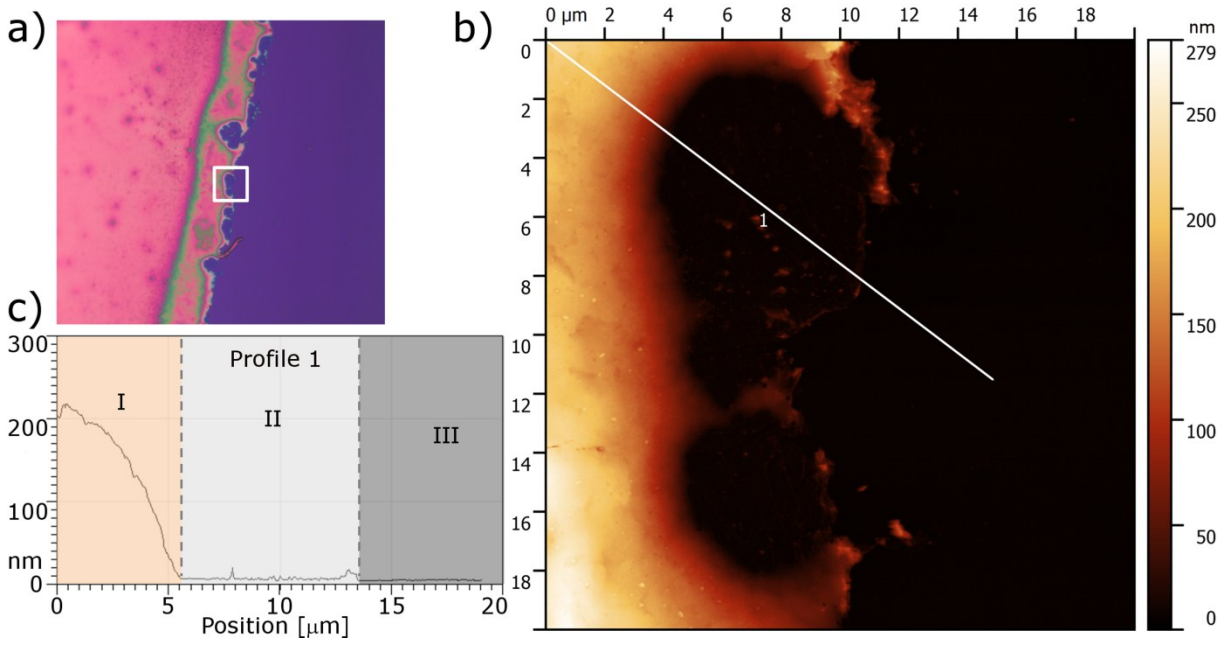

Figure S5. a) Detail of the optical picture (Figure 6-a in the main text) showing the region of the Pip@Gn sample in which the AFM measurement was performed (marked with white square). b) AFM of the "bay" feature of the sample were part of the graphene is not covered by the perovskite. The image was acquired close to the graphene edge showing both perovskite film and the graphene monolayer on Si/SiO_2 substrate. c) Height profile extracted from the marked region. The perovskite layer thickness was estimated to roughly 200 nm and decreasing steeply at the edge (region I). Defective graphene sheet is also visible in the profile with a thickness lower than 1 nm (region II) while the last region of the profile (III) shows bare Si/SiO_2 substrate).

Optical pictures of perovskite morphology

2D perovskites deposited on different substrates

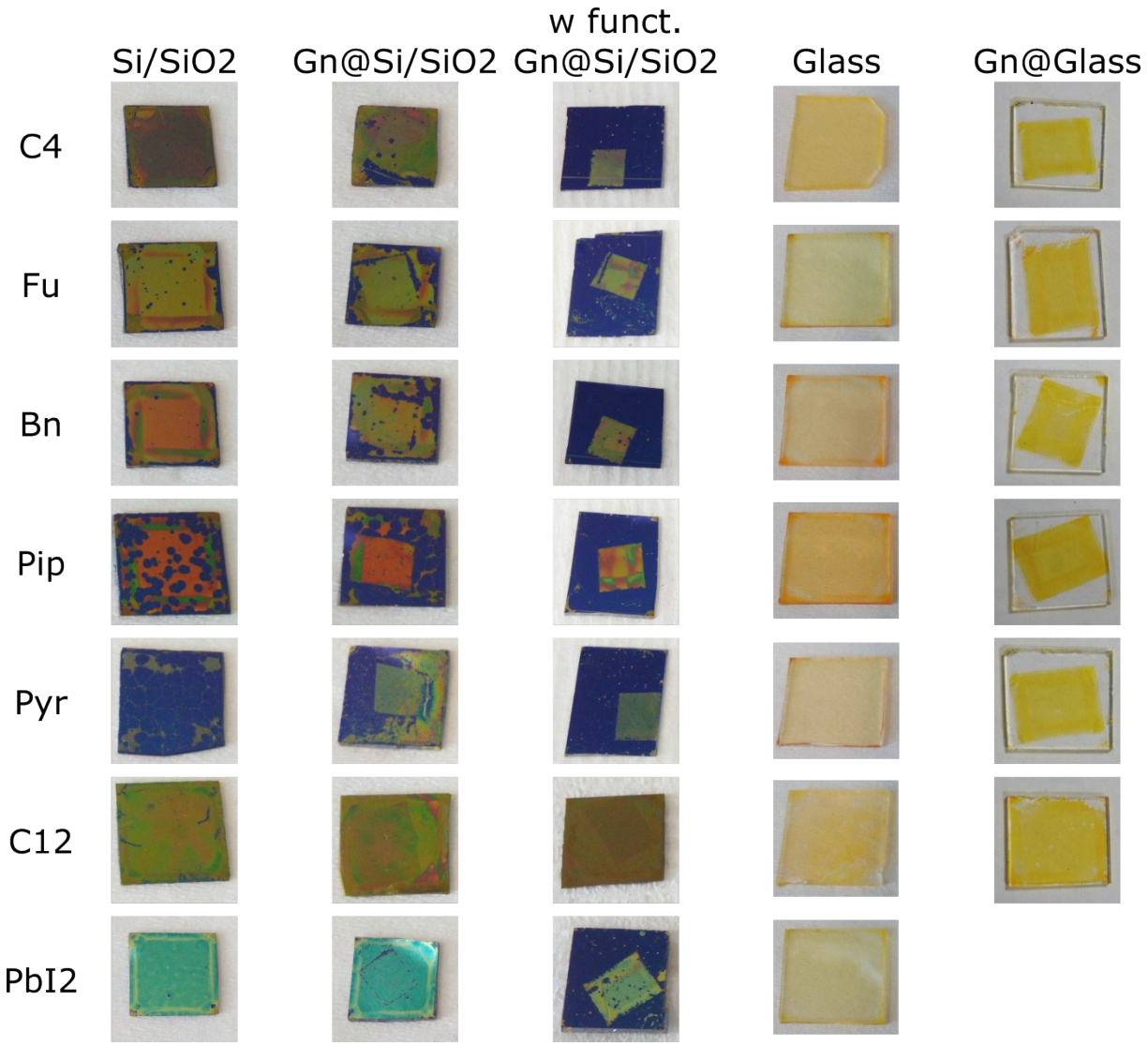

Figure S6. Photos of perovskites (+ lead iodide as reference) deposited on different substrates which (in order from left to right) are: bare Si/SiO_2, graphene on Si/SiO_2, graphene on functionalized Si/SiO_2, plasma treated glass, graphene on glass. As it is visible in the pictures there is a trend of increase in selectivity already when changing the organic precursor of the perovskite but the most remarkable result is obtained with endcapping of the Si/SiO_2.

Pip perovskite on patterned graphene

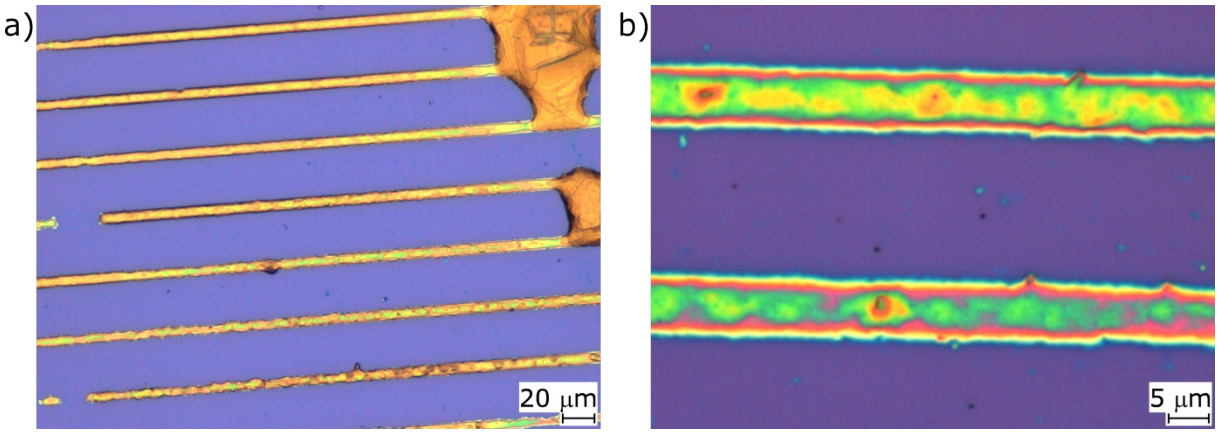

Figure S7. Optical microscope pictures of **Pip** perovskite assembled on patterned graphene after the endcapping of the SiO_2. The pattern was made by photolithography and plasma etching of the transferred graphene on Si/SiO_2 substrate.

3D perovskite on graphene

It was tested if the increase in selectivity achieved by the functionalization of the substrate was effective also in the case of the growth of 3D perovskite ($CH_3NH_3PbI_3$). Preliminary results show that in principle the method is transferable even though the 3D perovskite is more sensitive to the ambient conditions and needs more optimization. Solution of MAI:PbI_2 in 1:1 ratio was drop casted from DMF taking advantage of the different wettability induced by the functionalization. After the annealing at 100°C, PMMA solution in chloroform was spincoated on top of the sample as protective layer, then XRD were measured to confirm the structure (see Figure S3 in section "XRD").

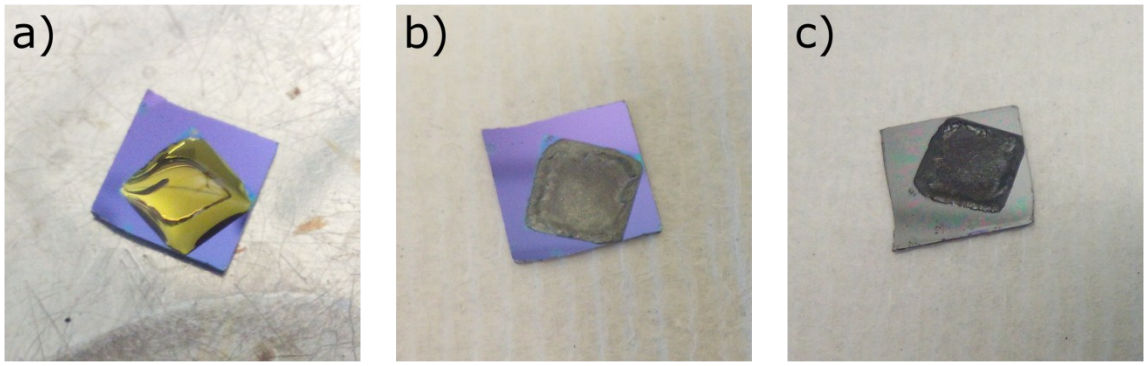

Figure S8. Camera pictures of the 3D perovskite drop casted on graphene after functionalization of the Si/SiO_2 surface. a) as casted, b) after annealing at 100°C, c) after spincoating of PMMA solution in chloroform.