Embedded-grid silver transparent electrodes fabricated by selective metal condensation

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Experimental Procedures

PFDMA synthesis. PFDMA was synthesised according to the literature procedure (S.-H. Jung, *et al.*, *J. Polym. Sci., A: Polym. Chem.*, 2018, **56**, 2672–2680.)

Master fabrication. A silicon master with square grids was produced by standard photolithography: a clean silicon wafer was spin coated with a uniform layer of photoresist (S1818, 300 rpm for 5 s and 4000 rpm for 20 s); after baking at 115°C it was exposed to ultraviolet light (130 mJ/cm^2) under a chromium/quartz mask and developed in MF319 developer for 35 s. The patterned photoresist layer was used as a mask for the etching process and then was removed. The final grids had line width, a ~ 1.7 μm, spacing w ~11-24 μm and height h ~ 1.7 μm. The master was coated with a (1H,1H,2H,2H-perfluorooctyl)trichloro silane (FTS) layer deposited from the vapour phase at a low pressure to help replica detachment. This first step was performed just once and then the master could be replicated several times.

Polydimethylsiloxane stamp. The silicon master was replicated with polydimethylsiloxane (PDMS, Sylgard 184) to produce the stamp for the microcontact printing procedure. Base and curing agent were mixed (10:1 w/w), degassed and poured onto the master. After curing at ~60°C for at least 6h the polymerised stamp was gently peeled off the master. The relief structures on the PDMS stamps have a square base with rounded corners. The side of the squares is w=11.3±0.2 μm or w=24.2±0.5 μm and the distance between two squares is a=1.7±0.2 μm. The corresponding nominal fraction of metal (the fraction in case the squares had not had round corners) is f=24.4%, and f=12.7% respectively.

Substrate cleaning. Glass substrates (12×12 mm or 18 × 18 mm) were cut from 1.2 mm thick glass microscope slides (Academy) and PET substrates (12 × 12 mm, 18 × 18 mm or 25×25 mm) were cut from a roll (Hostapan GN4600, MITSUBISHI POLYESTER FILM). These types of substrates were cleaned by ultra-sonic agitation in a diluted solution of surfactant, deionized water and IPA for 30 min each. After drying with a stream of nitrogen, glass and PET slides were treated with UV/O_3 cleaner respectively for 15 and 10 minutes to raise the surface energy.

Adhesive layer (optional). Immediately after cleaning, the PET substrates were coated with a layer promoting metal adhesion (i.e. with a condensation coefficient of 1): 0.3% w/v PEI/water solution was spin coated at 5000 rpm for 30 s, then substrates were annealed at 100 °C for 20 minutes[16].

Micro-contact printing. The ink was a 2-4% w/w poly(1H,1H,2H,2H-perfluorodecylmethacrylate) (PFDMA) in hydrofluoroether solvent (HFE-7500, 3 M) solution. The ink was spin-coated on the PDMS stamp at 2000 rpm for 30 s. The stamp was gently put in contact with the substrate, without applying any extra pressure, for at least 10 s.

Metal evaporation. Ag was deposited directly onto the printed surfaces by thermal evaporation (thickness 40-100 nm, rate 0.2-2.7 Ångstrom per second).

UV/O treatment. After annealing, electrodes were exposed under UV/O_3 for 5 minutes. This step is necessary to increase the surface energy of the fluorinated features to improve the wetting of other coating layers.

Acetic acid. The UV/O_3 treatment leaves a very thin layer of Ag_2O on the Ag grid which can be removed by washing the electrodes in acetic acid for 30 s and drying with nitrogen. Notably, as well as the tiny Ag nanoparticles on the surface of the PFDMA, the silver grid is also oxidized and etched during the UV/O_3 and acetic acid treatment. However, the Ag grid sheet resistance is increased by ≤ 6%, and so only the top few percent of the Ag grid is oxidised and removed.

Coatings. The grid electrodes can be uniformly coated after the UV/O treatment and the optional acetic acid rinsing. The coating was demonstrated for three materials commonly used in the fabrication of organic photovoltaic devices:

1. PEDOT:PSS (poly(3,4-ethylenedioxythiophene) PH1000 by Ossila) with 5% v/v CAPSTONE FS-30 (Apollo Scientific) was spincoated on the electrode at 5000 rpm for 60 seconds and then annealed at a temperature higher than 100°C for at least 10 minutes. CAPSTONE FS-30 is a fluoro-surfactant essential to obtain a uniform wetting of PEDOT:PSS on the surface of the electrode.

2. PEDOT:PSS (poly(3,4-ethylenedioxythiophene) HTL Solar 3 by Ossila) in toluene was spincoated on the electrode at 5000 rpm for 60 seconds and then annealed at a temperature higher than 100°C for at least 20 minutes.

3. Aluminum-doped zinc oxide ink for spin coating/slot-die coating (Sigma-Aldrich) was spincoated on the electrode at 1250 rpm for 30 seconds and then annealed at a temperature higher than 100°C for at least 5 minutes.

Morphological and elemental characterization of patterned samples. Atomic force microscopy (AFM) imaging was performed using an Asylum Research MFP-3D operated in tapping mode to study the morphology of the printed substrates and the patterned metal layers. The height of the FTS features and the depth of the apertures was evaluated using IgorPro. Scanning electron microscopy (SEM) imaging was performed using ZEISS Gemini500 with an accelerating voltage of typically 2-10 kV to evaluate the presence of metal particles inside the holes and the compactness of the continuous metal layer. EDXS spectra were recorded using an Oxford Instruments Si-Li detector unit on the SEM instrument, at an accelerating voltage of 6 or 10 keV. Far-field total and scattered transmittance of patterned metal films were measured over the wavelength range of 300–1100 nm using a 150 mm Spectralon Integrating Sphere coupled to PerkinElmer LAMBDA high performance series of UV/vis spectrometer. The incident beam passed through the substrate first.

Calculation of metal condensation coefficient *C*: *C* was calculated from the integral of the metal peaks in EDXS spectra recorded using an Oxford Instruments Si-Li detector unit on the SEM instrument, at an accelerating voltage of 6 keV. C is a value relative to a reference surface considered to have C=1, i.e. where all the metal atoms arriving at the surface are adsorbed. For grids, the value of C is the ratio between the integral of the metal peak inside the square polymer layer and the integral of the peak of the metal layer deposited on the bare PET cross, acquired under the same conditions:

$$C = \frac{I\ (in\ the\ fluorinated\ square)}{I\ (in\ the\ cross)}$$

where I indicates the integral of the principal metal peak in the EDXS spectrum (see Fig. S1).

Bending Tests. Cyclic bending tests were performed on a bespoke bending test rig. The bend radius was 5 mm and bending frequency was 36 bends per minute. Testing was performed with the grid under tension. The sample size was approximately 2 × 2 cm.

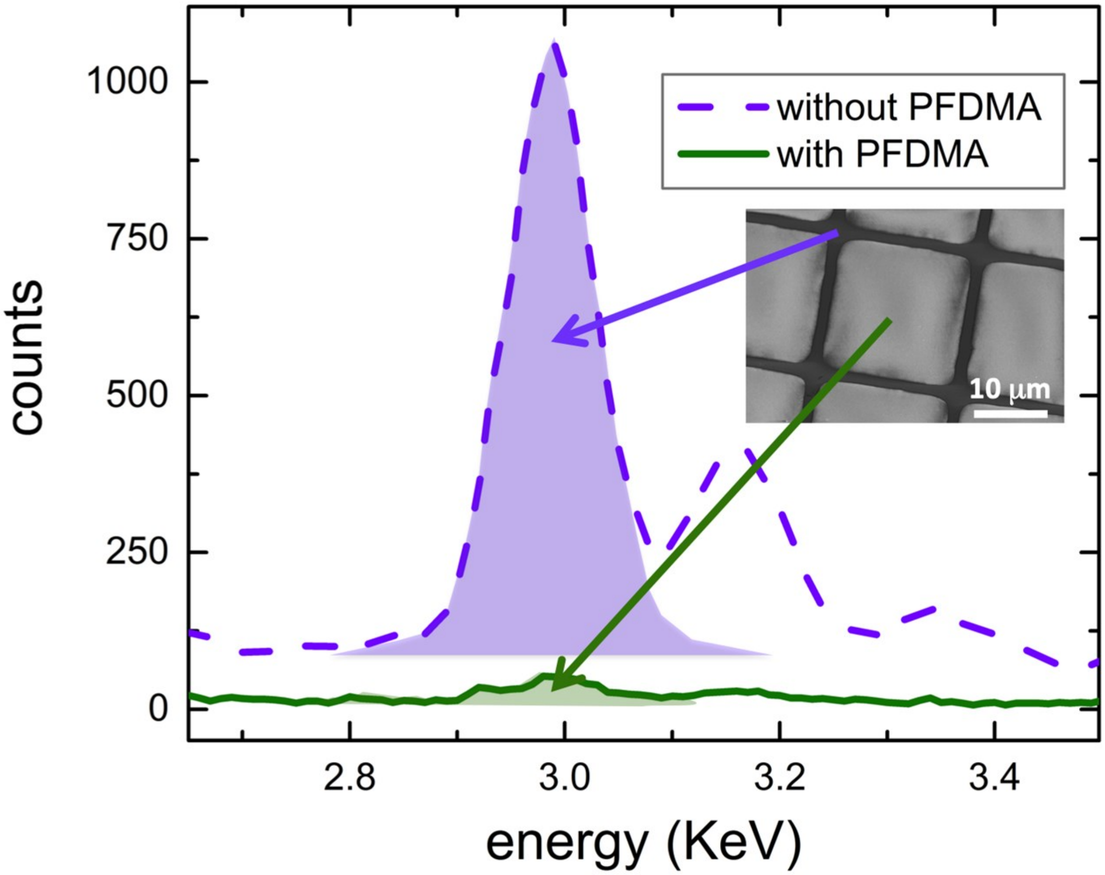

Figure S1. Ag EDXS spectra for the calculation of *C*. The three peaks refer to X-ray transitions Lα_1 (2.98 KeV), Lβ_1 (3.15 KeV) and Lβ_2 (3.35 KeV). *C* is the ratio between the amount of metal condensed on the PFDMA square (green) and the metal condensed on the bare cross (violet) evaluated from the intensity of the Lα_1 Ag EDXS peaks."

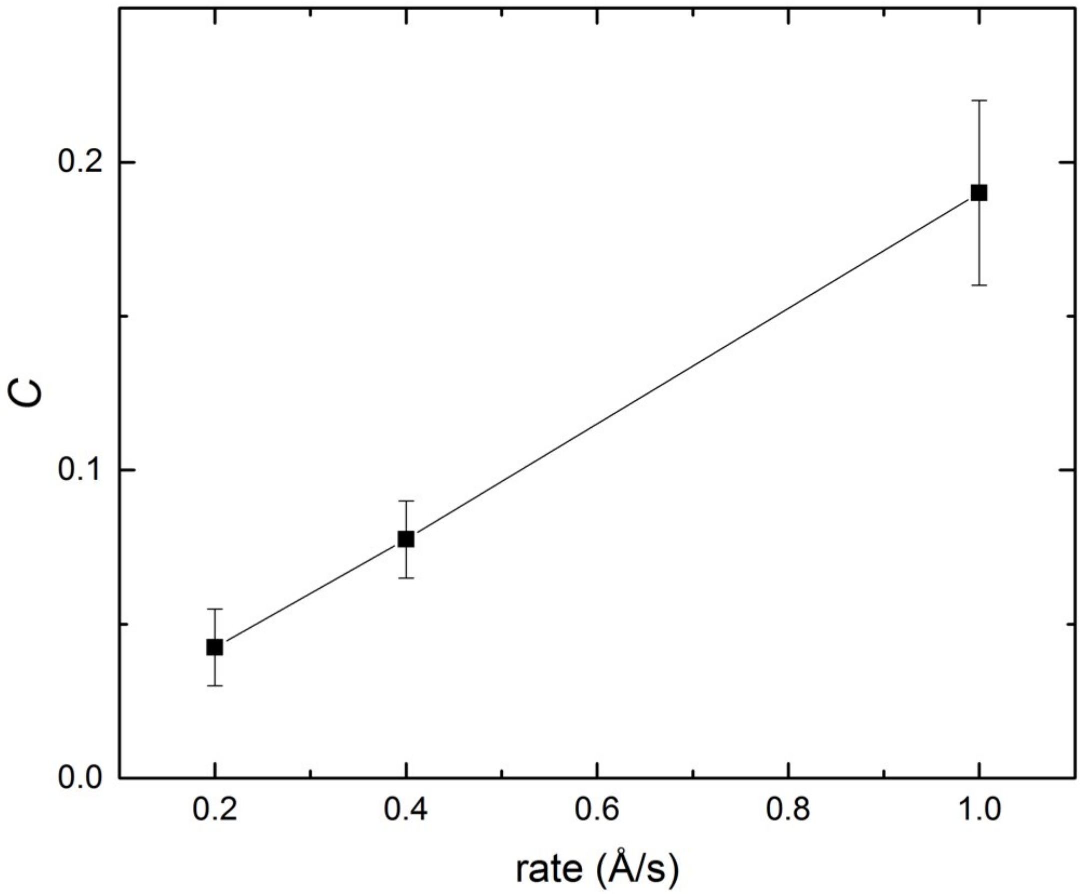

Figure S2. Condensation coefficient *C* on PFDMA as a function of the metal evaporation rate for silver, without heating the substrates during the metal evaporation. *C* is the ratio between the amount of metal condensed on the PFDMA layer and the metal condensed on the bare substrate evaluated from the intensity of the EDXS peaks. Error bars are the maximum error calculated from different samples.

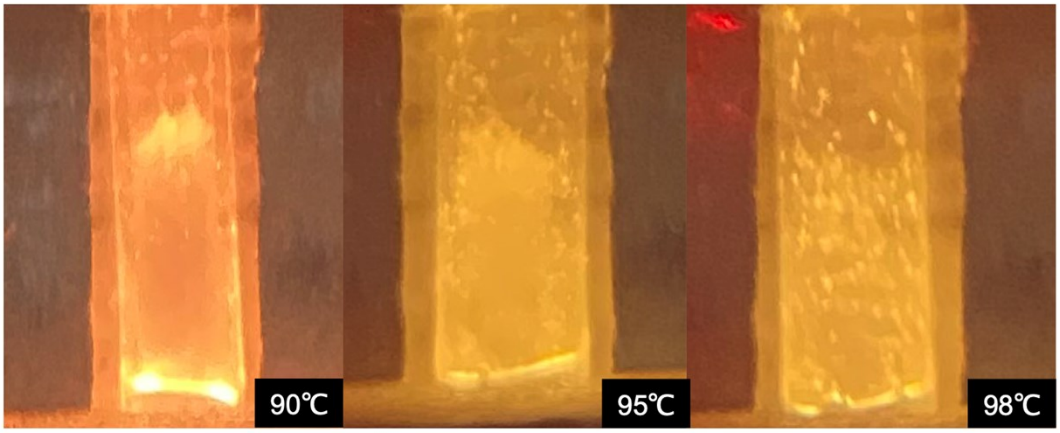

Figure S3. Melting point measurement of PFDMA. At around 90°C, the colour of the polymer got darker. When the temperature reached 98°C, PFDMA turned into a polymer melt which stuck on the capillary wall.

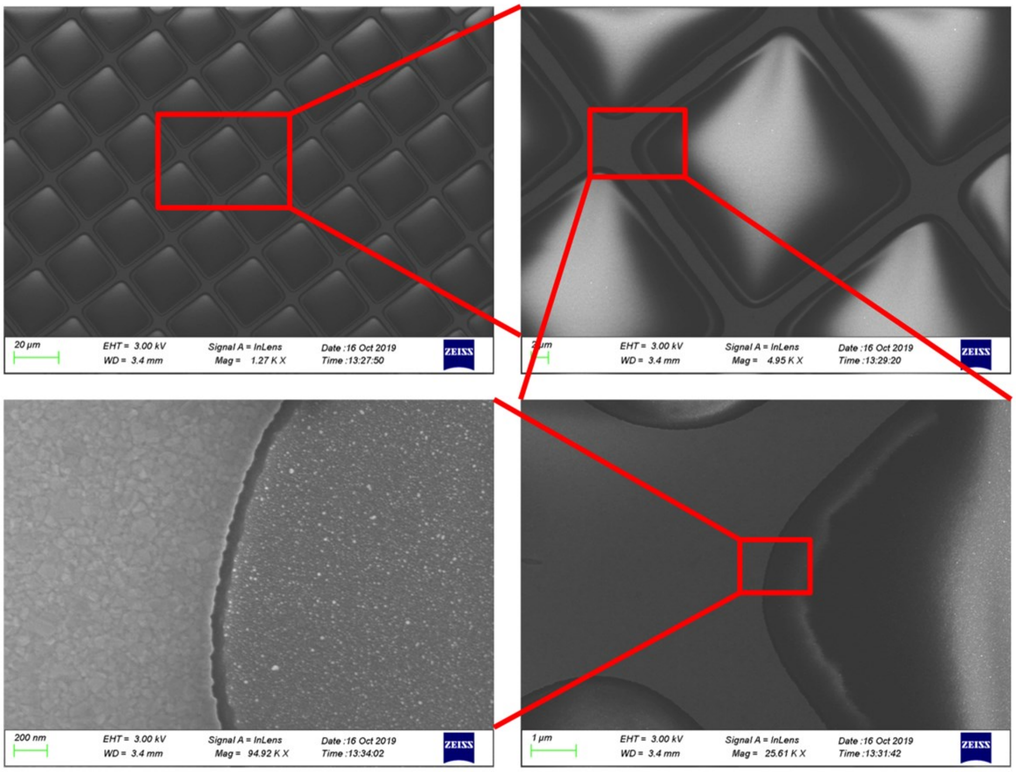

Figure S4. SEM images of a Ag grid produced by printing a PFDMA pattern of squares onto a glass substrate and evaporating 70 nm Ag. The grid lines are 1.7 µm wide and 70 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage.

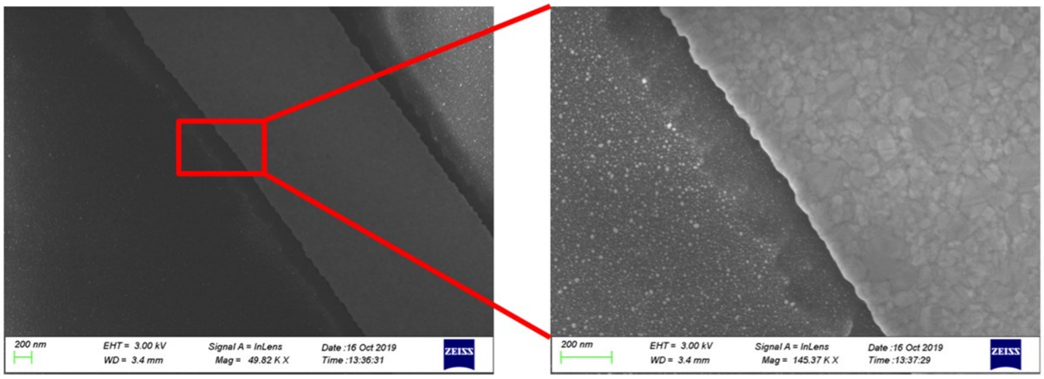

Figure S5. SEM images of a Ag grid produced by printing a PFDMA pattern of squares onto a glass substrate and evaporating 70 nm Ag. The grid lines are 1.7 µm wide and 70 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage.

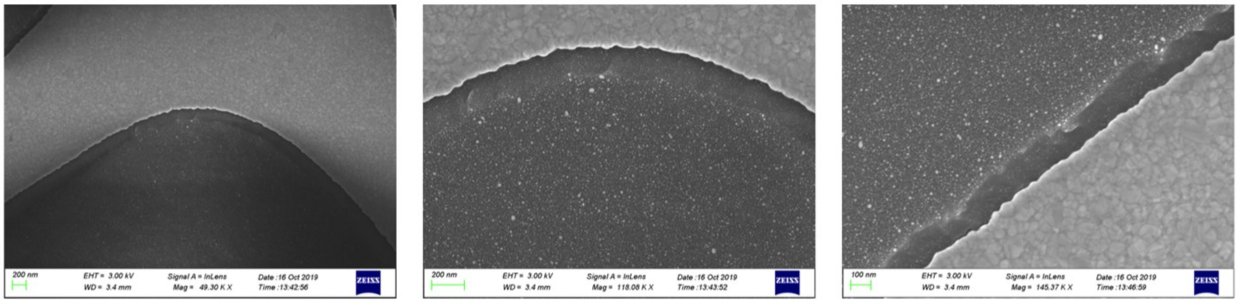

Figure S6. SEM images of a Ag grid produced by printing a PFDMA pattern of squares onto a glass substrate and evaporating 70 nm Ag. The grid lines are 1.7 µm wide and 70 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage.

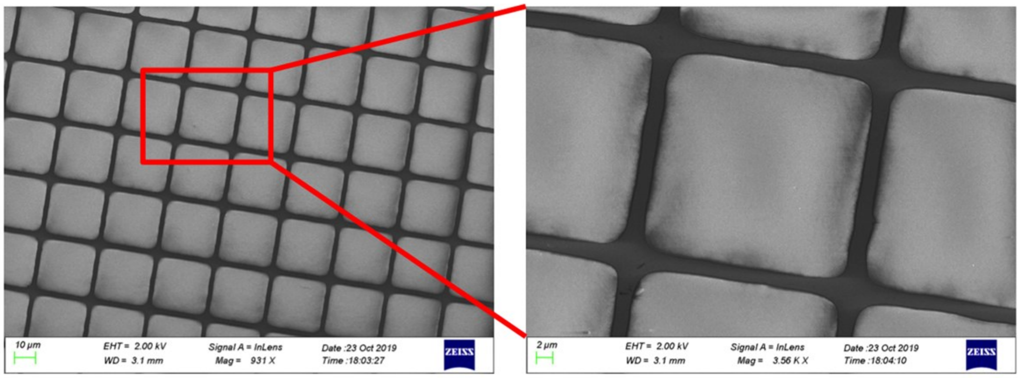

Figure S7. SEM images of a Ag grid produced by printing a PFDMA pattern of squares onto a PET substrate coated with PEI and evaporating 100 nm Ag. The grid lines are 1.7 µm wide and 100 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage.

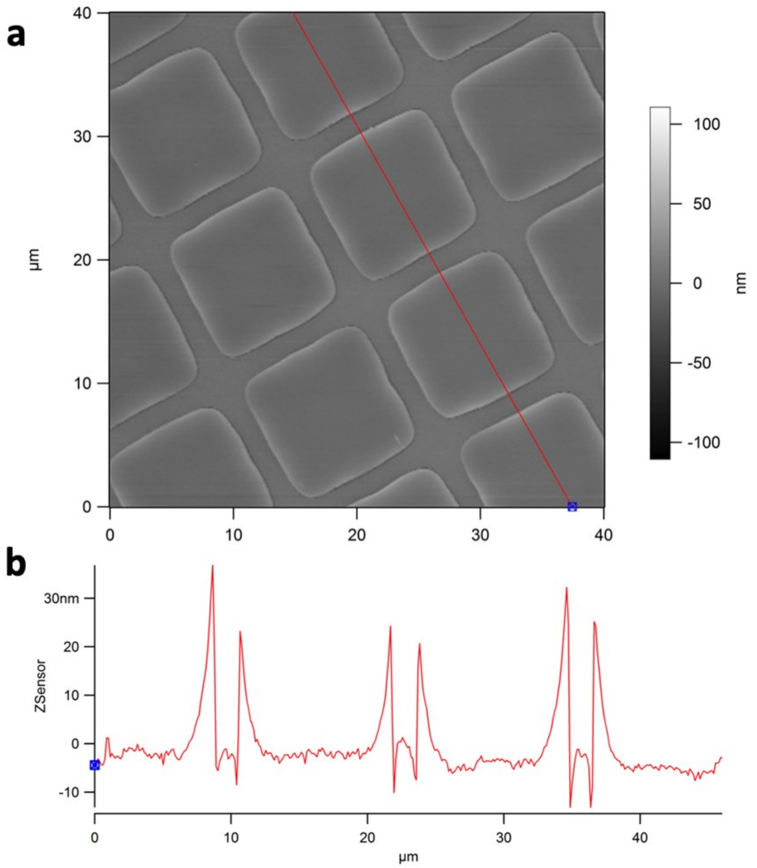

Figure S8. AFM image of a Ag grid produced by printing a PFDMA pattern of squares onto a glass substrate and evaporating 80 nm Ag. The grid lines are 1.7 µm wide and 100 nm thick. The grid spacing is 11.3 µm, which corresponds to 25% metal coverage. a) AFM scan and b) height profile along the line drawn in image a. Notably, at first glance the AFM cross-section makes the edge of the PFDMA layer where it interfaces the Ag gridlines look very sharp. However, the *x*-axis of this plot is on the scale of tens of nanometers and the *y*-axis is on the scale of micrometres so the 30-40 nm height increase occurs over several thousand nanometers, making it a very gentle rise rather than a sharp edge.

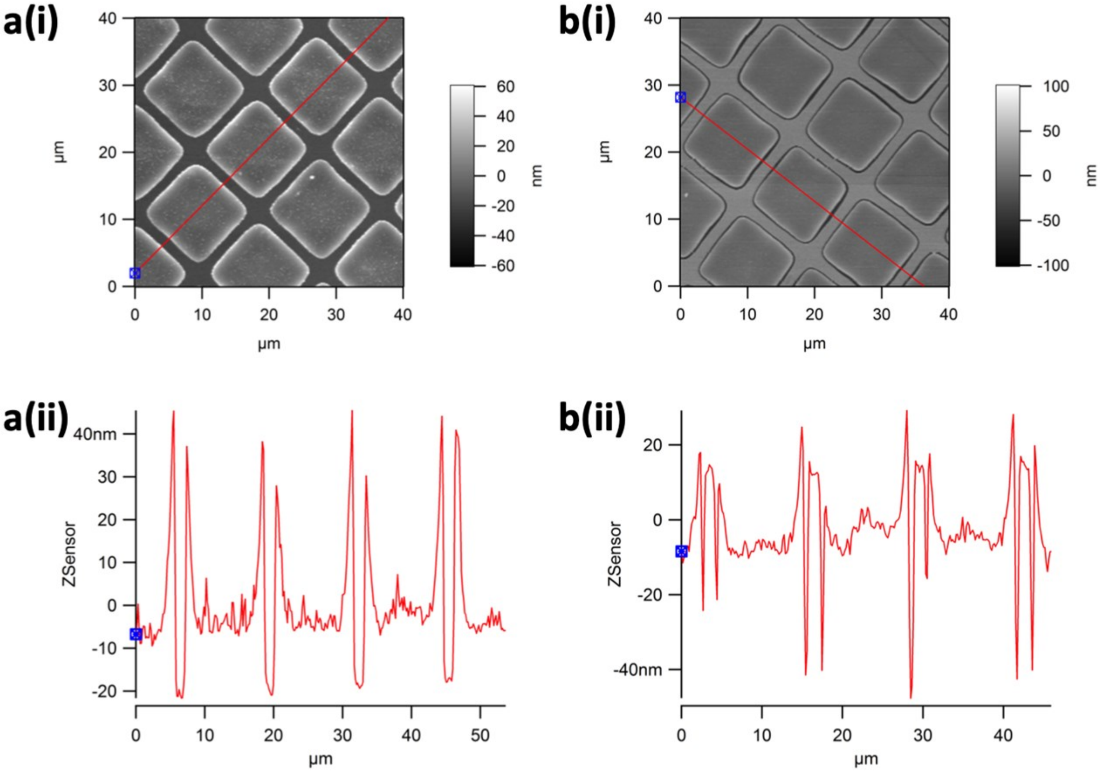

Figure S9. AFM images of a Ag grid produced by printing a PFDMA pattern of squares onto a glass substrate and evaporating 70 nm Ag. The grid lines are 1.7 µm wide and 100 nm thick. The grid spacing is 11.3 µm, which corresponds to 25% metal coverage. a) before and b) after 15 minutes UV/O treatment and rinsing in acetic acid for 30 s. (i) AFM scan and (ii) height profile along the line drawn in image (i).

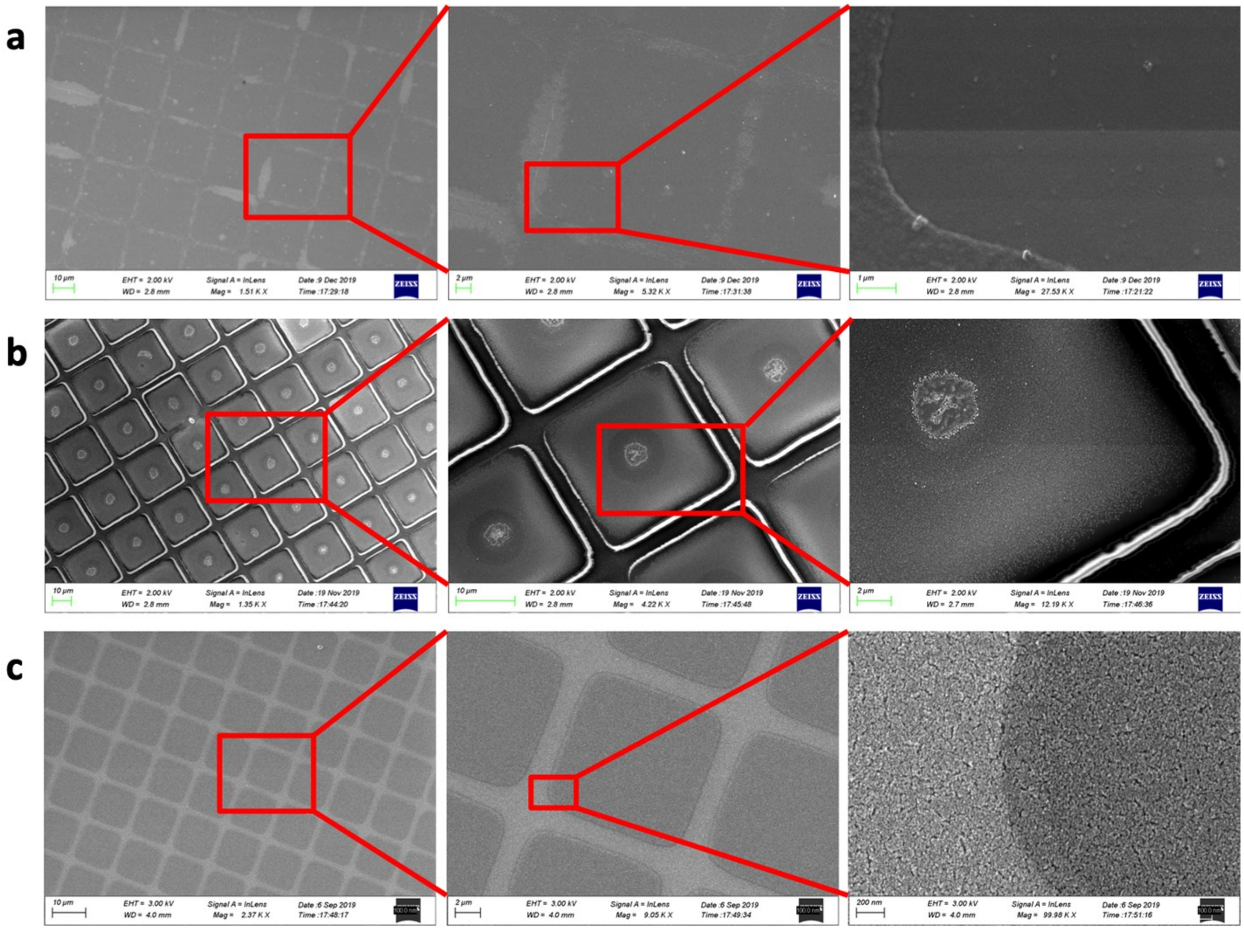

Figure S10. SEM images of Ag grids coated with different layers. Grids are produced by printing a PFDMA pattern of squares onto the substrate and evaporating Ag. a) The substrate is PET coated with a PEI adhesion layer. Grid lines are 1.7 µm wide and 100 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage. The sample was coated with PEDOT:PSS PH1000 with 5% v/v CAPSTONE FS-30; b) The substrate is glass coated with PEI. Grid lines are 1.7 µm wide and 100 nm thick. The grid spacing is 24.2 µm, which corresponds to 13% metal coverage. The sample was coated with PEDOT:PSS HTL Solar 3. The non-uniform areas at the centre of the gaps between grid lines correspond to aggregations of tiny Ag nanoparticles that are initially evenly distributed across the PFDMA surface (giving rise to the brown tinge before brief UV/O$_3$ treatment). This only occurs when using the PEDOT:PSS formulation in toluene (HTL Solar 3) because it requires a longer and higher temperature annealing step than the other two over layer materials tested.; c) The substrate is glass. Grid lines are 1.7 μm wide and 80 nm thick. The grid spacing is 11.3 μm, which corresponds to 25% metal coverage. The sample was coated with aluminum-doped zinc oxide.