Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information (ESI)

for

Photoemission Spectroscopy Study of Structural Defects in Molybdenum Disulfide (MoS_2) Grown by Chemical Vapor Deposition (CVD)

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- ## S1. Chemical Vapor Deposition (CVD)

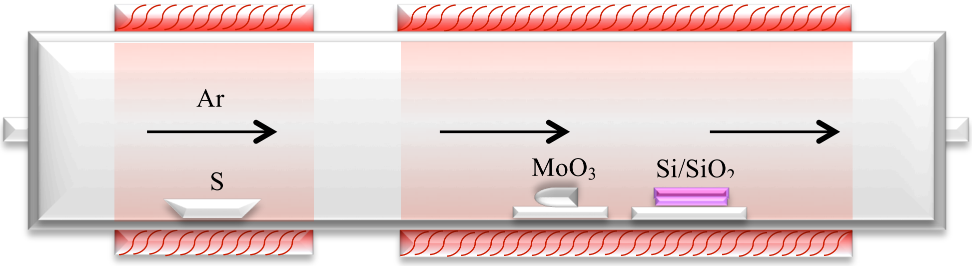

Figure S1 Scheme of the CVD setup used to grow MoS_2

CVD was carried out in a horizontal furnace (Model P330, Nabertherm). Two separate heating belts were used for S and MoO_3 for better temperature control as sketched in Figure S1. We used excess sulfur (powder, 99.998% pure, Sigma Aldrich) in a quartz crucible, 2-4 mg MoO_3 in a quartz cup (powder, 99.97% pure, Sigma Aldrich) and Ar (99.999%, Linde) as carrier gas. The CVD of MoS_2 on Si/SiO_2 (Prime Wafers) was performed at 700 °C for 10 minutes; thereafter the sample was left to cool, turning off the Ar gas when the temperature reached 560 °C.

- ## S2. Annealing of MoS_2

Annealing was carried out in the same furnace as CVD growth. We annealed the freshly grown MoS_2 in ambient pressure under 300 sccm Argon flow. We raised the temperature until 250 °C in 40 minutes and kept the samples at the maximum temperature for 2h.

- ## S3. Functionalization of MoS_2

Functionalization was performed following the procedure reported in the literature[1]. The annealed samples are first soaked for 72 hours in an aqueous solution prepared by dissolving 1 mg cysteine [Sigma Aldrich, purity 97%] in 10 mL MilliQ water. The samples are then rinsed three times with ethanol, acetone, isopropanol and water and blown dry with Ar. To remove any unbound cysteine molecules from the surface of the samples, we immersed again in ethanol for 45 minutes and rinsed again with ethanol, acetone, isopropanol and water before drying with an Ar flow.

- **S4. Optical Microscopy Images**

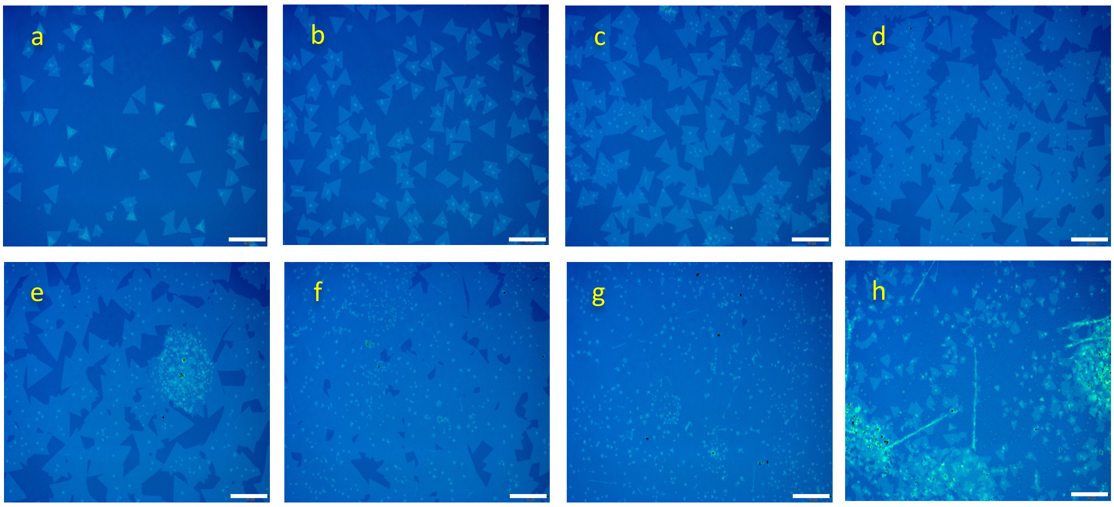

Figure S4 Optical microscopy images of as-grown MoS_2 in different regions of the substrate

As-grown MoS_2 crystals as seen under the optical microscope in different regions of the substrate are shown in Figure S4. The white scale bar corresponds to 20 μm. MoS_2 is seen in medium blue and SiO_2 in dark blue; the light blue and green contract in Fig. S4 (e) and (h) points to multilayer MoS_2. From the optical microscope images we conclude that we have MoS_2 flakes varying in size from several to tens of μm. In substrate regions close to the MoO_3 source the MoS_2 flakes have merged to form a continuous film, which fully covers the substrate. Specific regions were further characterized by atomic force microscopy (AFM); photoluminescence (PL), Raman and X-ray photoelectron spectroscopy (XPS).

- **S5. Atomic Force Microscopy and Raman Spectroscopy**

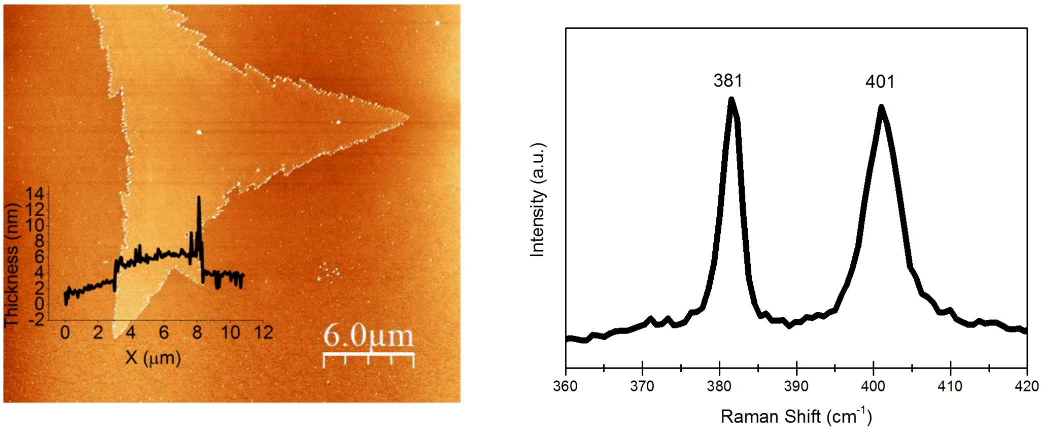

Figure S5 Left panel: Atomic force microscopy image of as-grown MoS_2; the inset shows the height profile. Right panel: Raman spectrum of as-grown MoS_2

Topography images were collected in tapping mode with a Scientec 5100 atomic force microscope, equipped with a silicon cantilever (BudgetSensors) with a 300 kHz resonant frequency and a force constant of 40 N/m and a Si tip. All images were analyzed using the WSXM program developed by Nanotech. Raman spectra were acquired with a µ-Raman Olympus U-TV1XC microscope, fiber-coupled to an Andor DV420A-BV detector, employing an excitation source with a wavelength of 532 nm. The laser beam size at the sample was about 10 µm and the laser power of 300 µW. Each spectrum was the average of 20 scans collected with an estimated 0.5 cm^{-1} resolution.

The AFM image and the Raman spectrum are shown in Figure S5. The height profile taken at the edge of the flake and shown in the inset of the AFM image, as well as the fact that the E_{2g} and A_{1g} lines are observed at 381 cm^{-1} and 401 cm^{-1}, respectively, confirm that we have single layer MoS$_2$[2–5]. All areas of the substrate, which showed up in medium blue in optical microscopy, gave rise to the same Raman spectrum corresponding to single layer MoS$_2$.

S6. XPS Measurements

The XPS measurements were carried out using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K_α X-ray source (hv = 1486.6 eV). The pressure in the measurement chamber was maintained below 1x10^{-9} mbar during data acquisition. The electron take off angle was 37° with respect to the surface normal. The diameter of the analyzed area was 600 µm^2 and the total energy resolution was set to 1.26 eV. The XPS binding energies are reported ± 0.1 eV and were referenced to the C1*s* core level binding energy of adventitious carbon at 284.8 eV. XPS spectra were analyzed using the least-squares curve fitting program WINSPEC, developed at the University of Namur, Belgium. Deconvolution of the spectra included a Shirley background subtraction and fitting with a number of peaks consistent with the structure of the film, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. Detailed spectra of the Mo3*d*, S2*p*, N1*s*, and C1*s* core level regions were acquired in 2-4 different spots to check for homogeneity.

Table S6

Region	**Peak**	**As grown**	**Annealed**	**Annealed and functionalized**
		BE (eV)	**BE (eV)**	**BE (eV)**
Mo3*d*	*i*-MoS$_2$	229.6	229.2	229.6
	d-1	231.3	230.8	231.2
	MoO$_3$	233.0	233.2	233.6
	d-2		231.6	232.0
	i-S2s	226.5	226.1	226.7
	d-S2s	227.6	227.2	227.7
	S-S			228.4
S2*p*	*i*-S2p	162.4	161.9	162.4
	d-S2p	163.1	162.6	163.2
	S-S			164.2

Table S6 summarizes the peak positions of all components in the XPS spectra.

- **S7. Wide Scan of XPS**

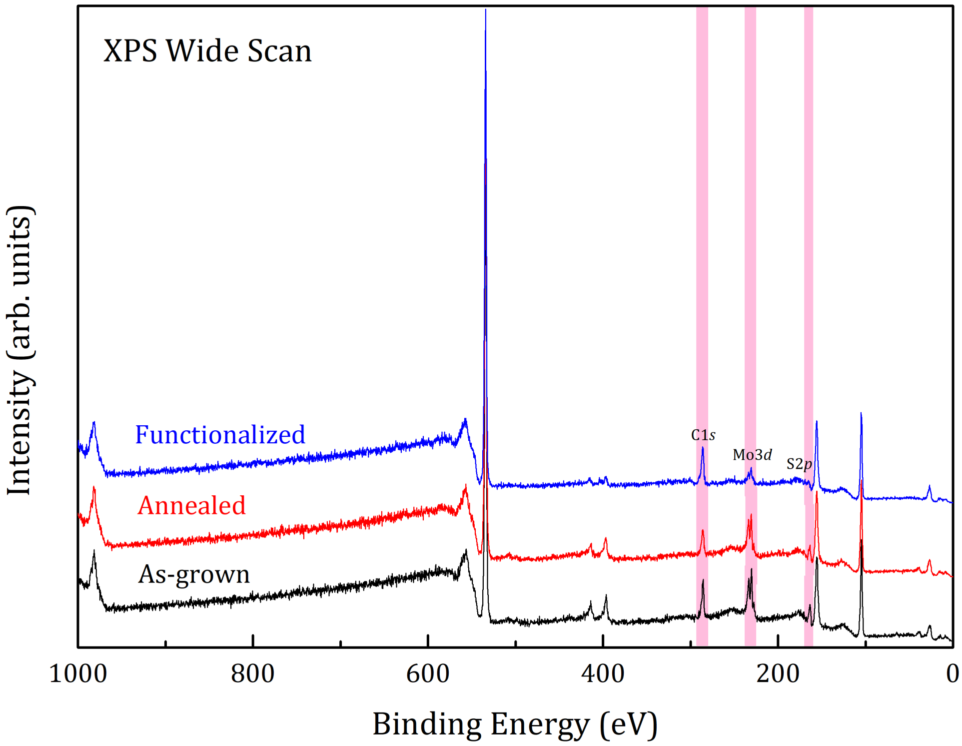

Figure S7 XPS survey spectra of as-grown MoS_2, and of annealed MoS_2 before and after functionalization with thiol-terminated cysteine

Figure S7 shows the survey photoemission spectra of as-grown MoS_2 before and after annealing and after functionalization with thiol-terminated cysteine of the annealed sample. The main peaks of the S2*p* and Mo3*d* core level regions are highlighted in pink. A decrease in S2*p* peak intensity was observed after annealing MoS_2 indicating successful sulfur desorption. In addition, an increase of C1*s* peak after functionalization also indicates the successful functionalization.

- **S8. Attenuated Total Reflection-Fourier Transform Infrared and Photoluminescence Spectroscopy**

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was performed with a Bruker VERTEX 70 spectrometer. Each spectrum was the average of 16 scans, collected with a resolution of 4 cm^{-1}. Data analysis and background correction was done with the OPUS spectroscopy software version 7.0.

The PL spectra were acquired with an ANDOR SR-500i-D1-R spectrometer, equipped with a 600 l mm^{-1} grating and coupled to an ANDOR DV420A-OE CCD camera. The laser excitation source had a wavelength of 532 nm, the beam size at the sample was about 10 µm and the laser power of 0.3 mW. The spectral resolution was 0.5 nm. Each spectrum was recorded with 1 s acquisition time to avoid a local overheating induced by the laser.

- **S9. Cystine functionalization**

To exclude the possibility of physisorbed dimers present after our cysteine functionalization method, we carried out the control experiment of cystine functionalization on MoS_2 using the same procedure. Based on the XPS results as depicted in Figure S9. We found that there was no significant spectral lines change in Mo3*d* peak before and after functionalization using cystine molecules. As we expected, no covalent functionalization occurred because cystine molecules don't have any thiol group to attach to MoS_2.

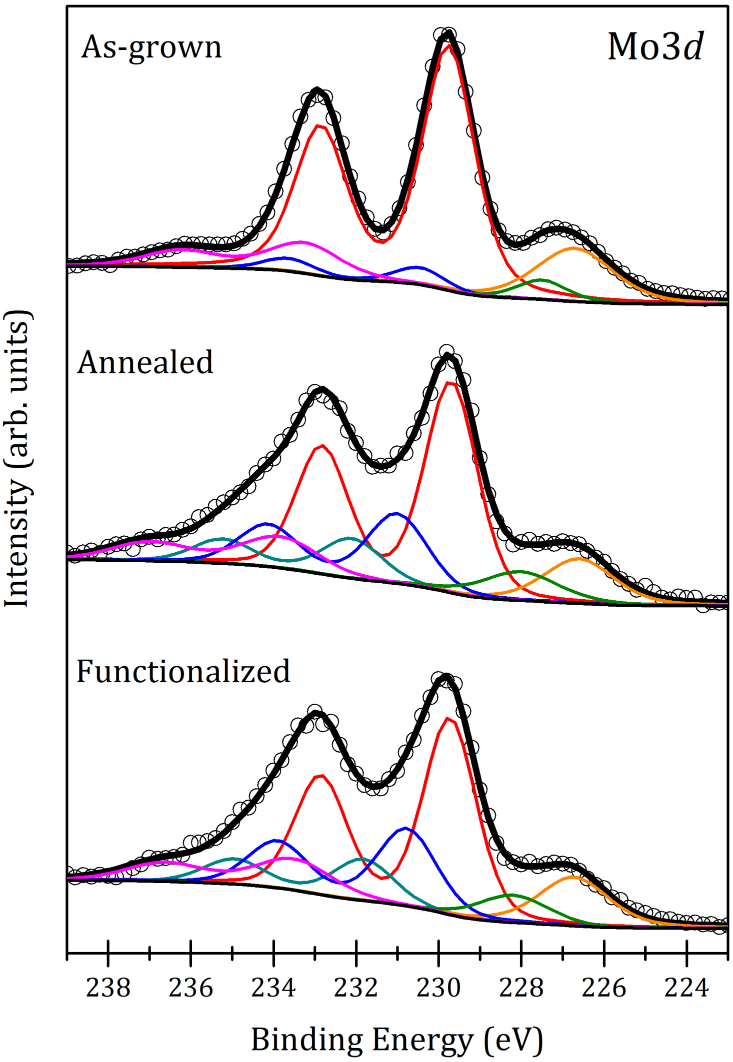

Figure S9

- **S10. The functionalization of as-grown MoS_2**

In our study, the defective MoS_2 (more sulfur vacancy induced by annealing) samples were used to achieve covalent functionalization. Direct functionalization of as-grown MoS_2 did not give any undisputable evidence for the presence of cysteine molecules.

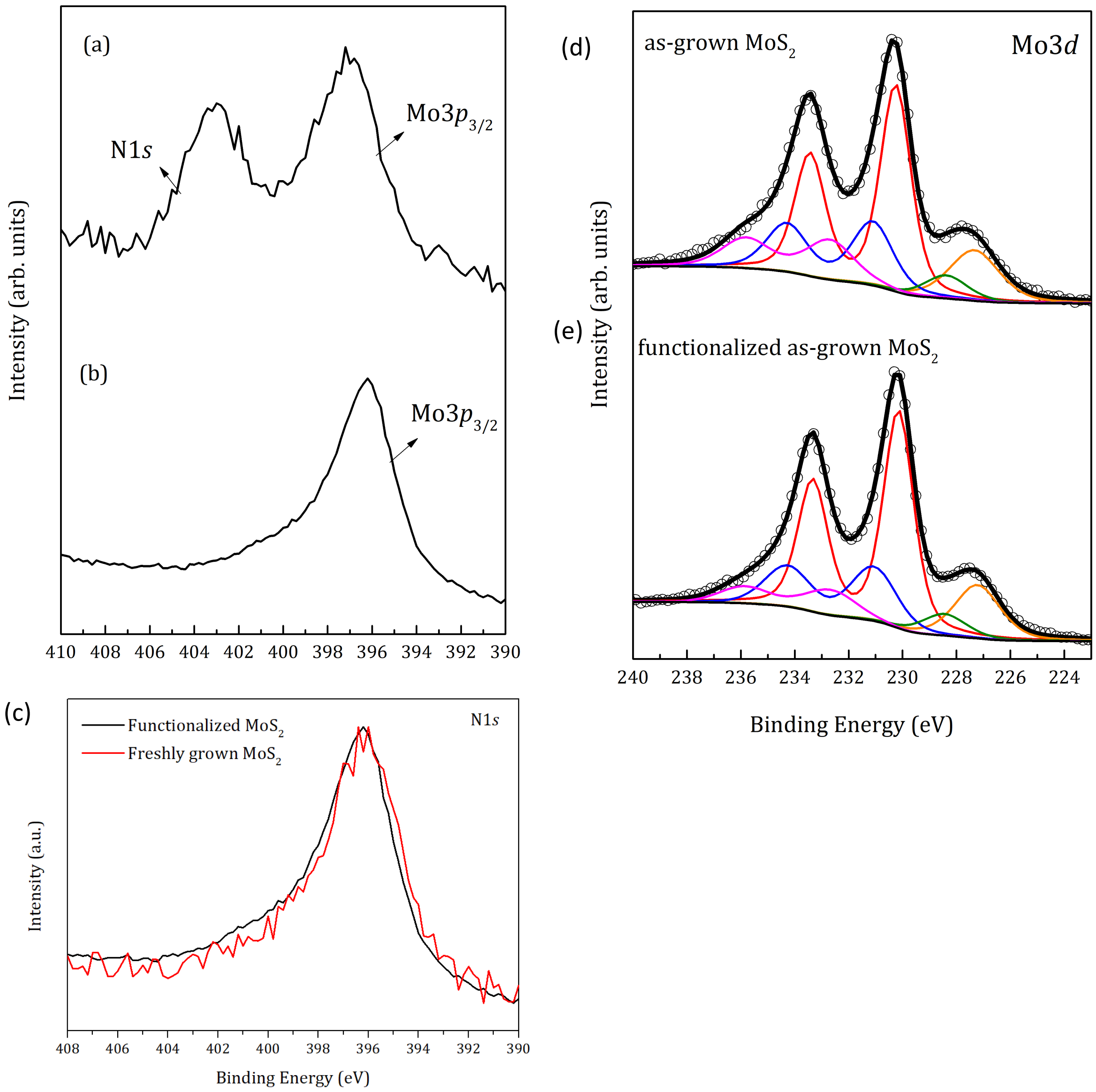

Figure S10 XPS spectra of the N1*s* core level region of (a) annealed MoS_2 after functionalization with thiol-terminated cysteine, (b) as-grown MoS_2 after functionalization with thiol-terminated cysteine; (c) superimposed XPS spectra of the N1s core level region of as-grown MoS_2 before and after functionalization with thiol-terminated cysteine. XPS spectra of the Mo3*d* core level region of as-grown MoS_2 before (d) and after (e) functionalization with thiol-terminated cysteine.

Figure S10 shows the XPS spectra collected after functionalization of annealed MoS_2 and before and after functionalization of as-grown, not-annealed MoS_2. The spectra of the Mo3*d* core level region of the as-grown, not-annealed MoS_2 before and after functionalization looked similar except for a very small decrease in intensity of the d(1)-Mo^{4+} hinting to a small amount of cysteine functionalization. Unfortunately, the small N1*s* cross-section makes it impossible to reliably detect N from the cysteine molecules in the functionalized as-grown MoS_2 (see comparison Fig. S10 (c)). We attribute this lack of success of functionalizing the as-grown sample to the fact that the S vacancies are quite reactive and tend to adsorb gas molecules from the environment as observed in the XPS results (see S7 above), in agreement with other reports [6–8]. The adventitious carbon contamination present in our samples was considerable (more than ~20%, see the XPS survey scan in S7). This hinders the functionalization with cysteine molecules because less active sites remain available on the surface.

- **S11. Photoluminescence spectra of annealed MoS_2**

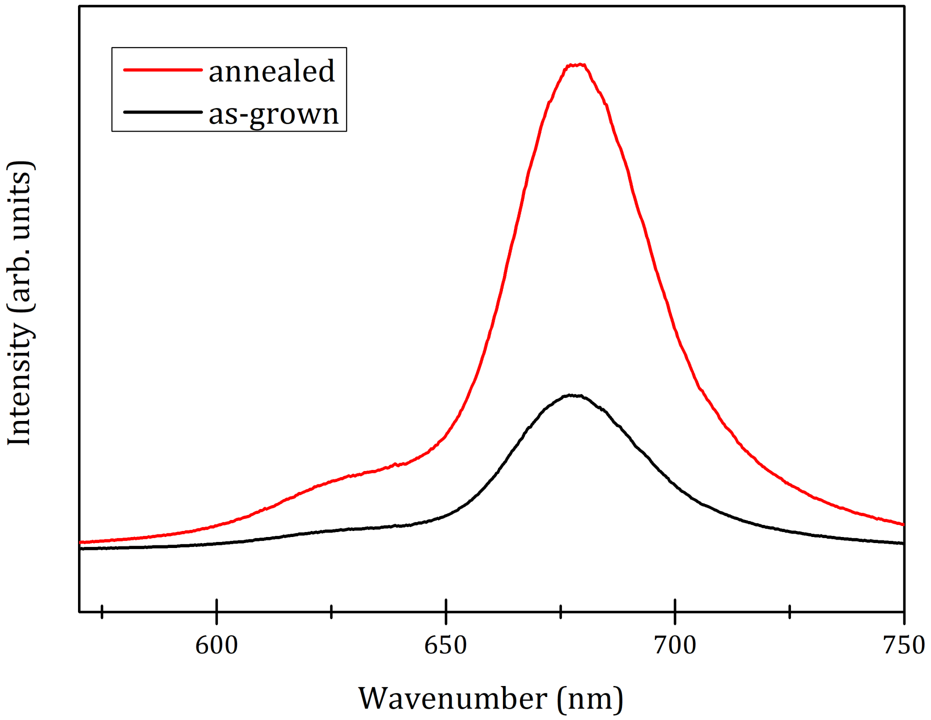

Figure S11 Photoluminescence spectra of as-grown and annealed MoS_2.

After annealing, the PL intensity increased due to the removal of physisorbed contaminants, in good agreement with the previous reports [9,10].

References

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