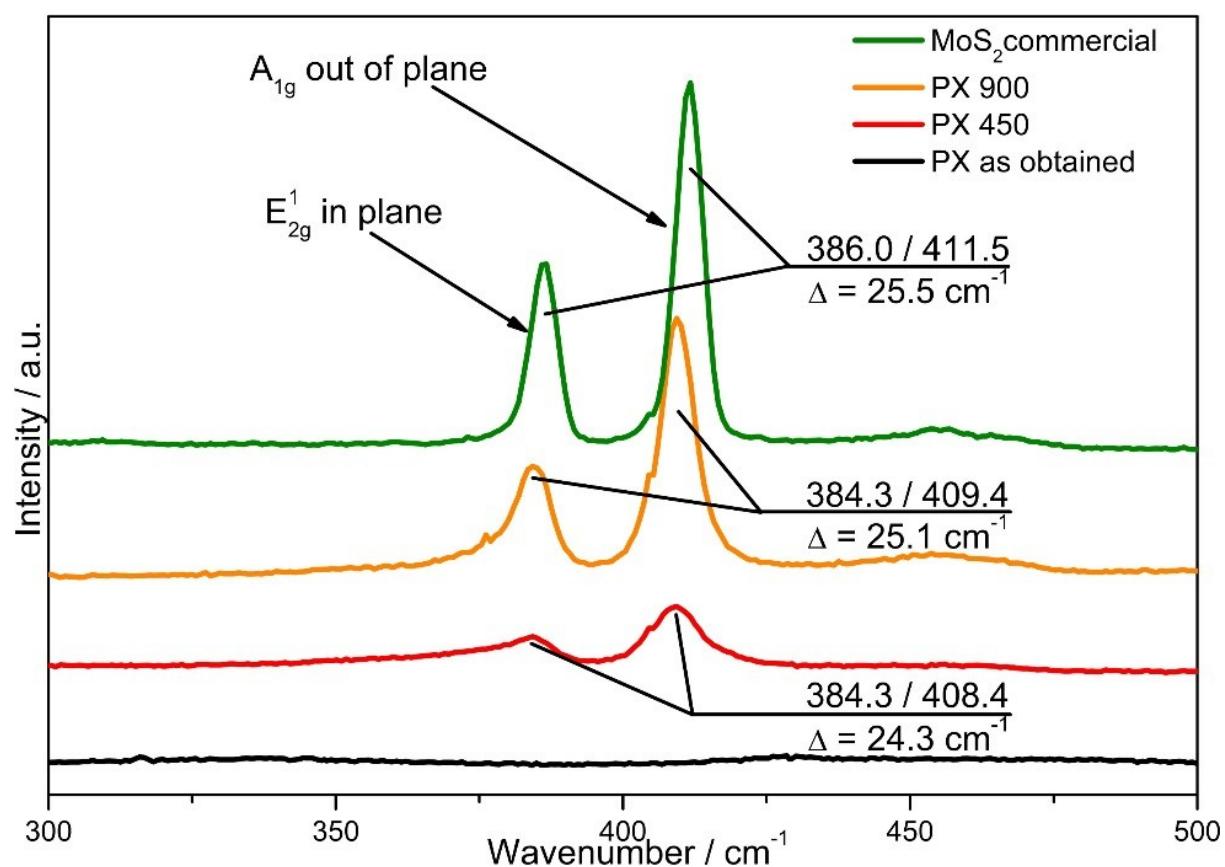


## Supporting Information

### Room Temperature Synthesis of an Amorphous Molybdenum Sulfide Based Composite: Characterization and Photocatalytic Hydrogen Evolution.

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#### 1. Raman measurements



**Figure S1.** Raman spectra of PX (black trace), PX450 (red trace), PX900 (orange trace) and commercial MoS<sub>2</sub> (green trace).

## 2. Infrared measurements

Figure S2 shows the MIR spectra of PX, ATM, hydrazine and ammonia for comparison. If residues of the starting material ATM are still in the sample vibrations of  $\text{NH}_4^+$  in the MIR and  $\text{MoS}_4^{2-}$  in the MIR and FIR regions should be observable. Comparison of the MIR spectra of ATM and PX demonstrates that the intense absorption of the  $\text{MoS}_4^{2-}$  ion is absent in PX. But some other broad bands can be observed although not very intense and quite broad which renders the assignment rather difficult: the band at  $1580 \text{ cm}^{-1}$  can be assigned as the deformation vibration of a  $\text{N-NH}_2$  group,  $1400 \text{ cm}^{-1}$  fits with the deformation vibration of  $\text{H-N-H}$ , and the weak band at  $986 \text{ cm}^{-1}$  may be assigned to the N-N vibration of a  $\text{Mo-NH}_2\text{NH}_2$  group.<sup>1</sup> Note that the intensities of the absorptions in Figure 8 are normalized (against the peak with the highest intensity) and without this normalization the bands of PX were not visible due to a very low intensity indicating a low concentration of N species in PX.

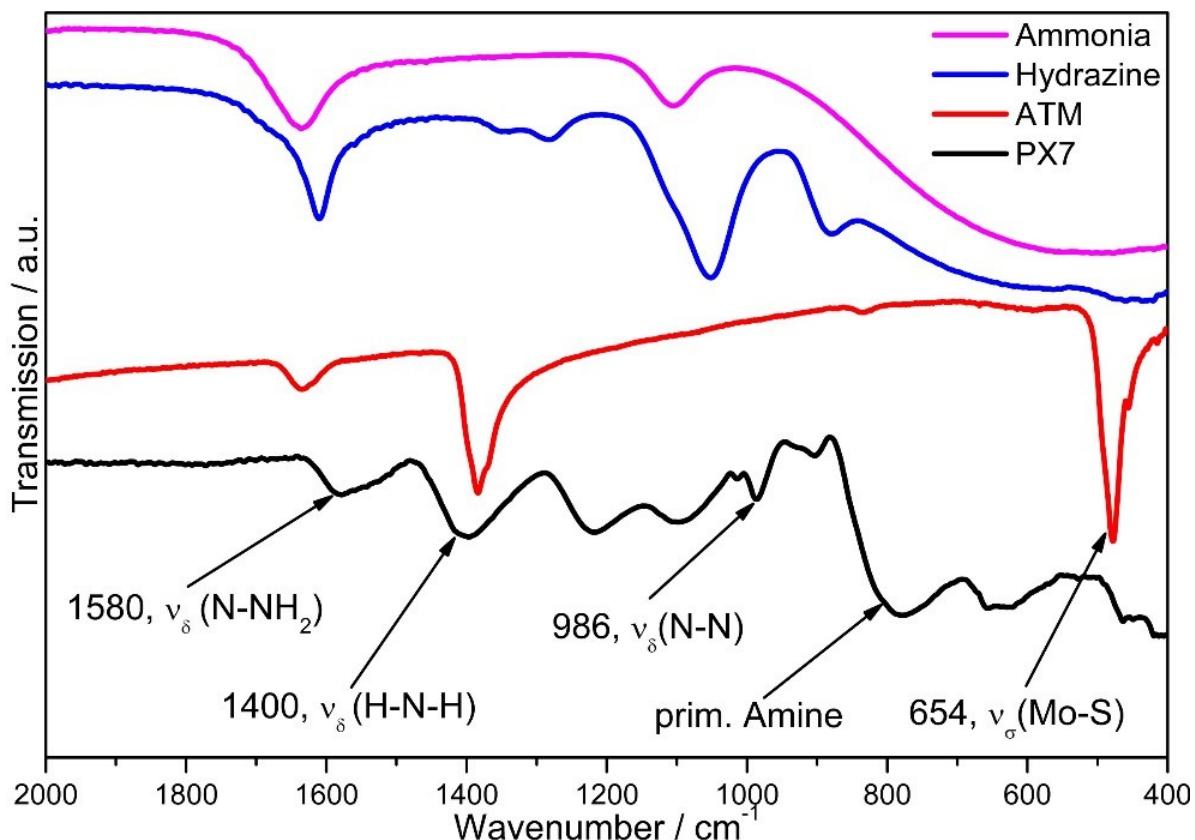
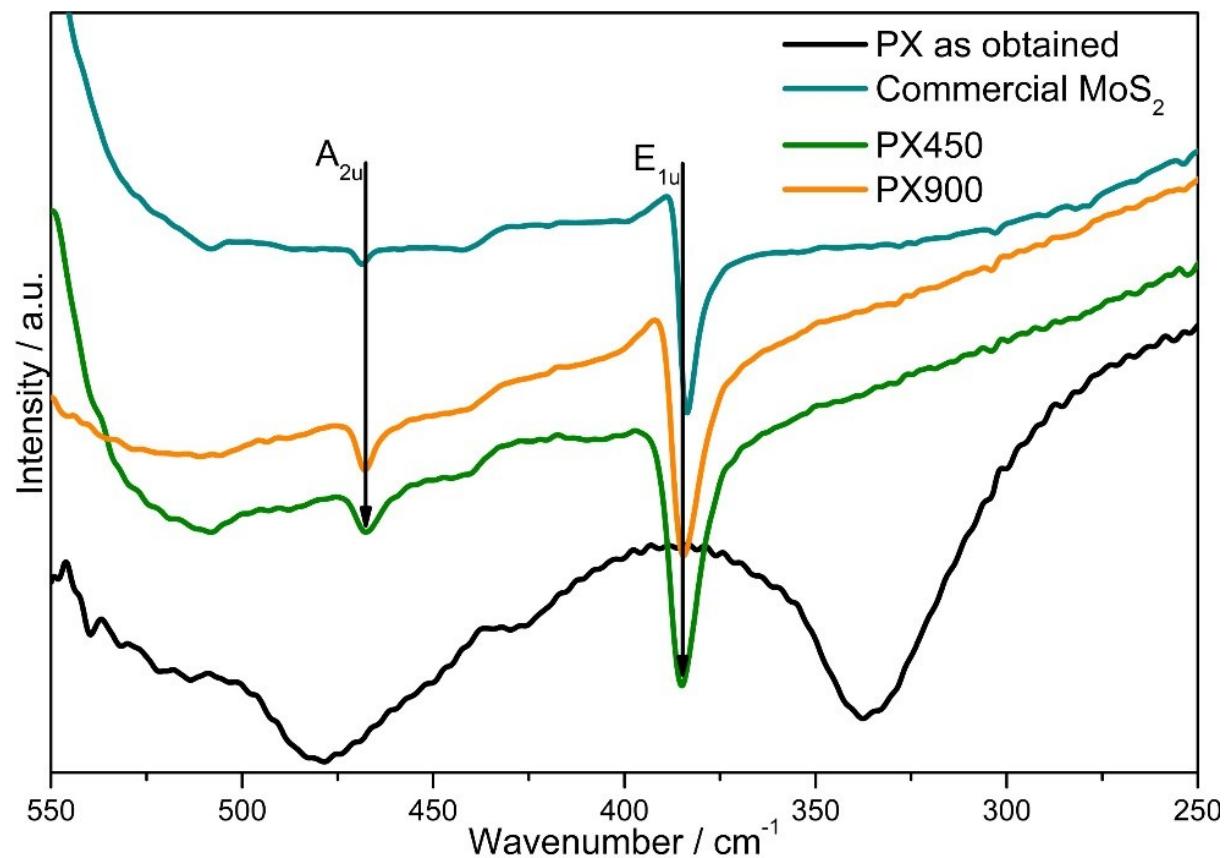


Figure S2. Comparison of the MIR spectra of PX (black trace), ATM (red trace), hydrazine (blue trace), and ammonia (purple trace).

A distinct assignment of the remaining absorptions is not straightforward due to the broadness of the bands. In any case, the vibrational spectroscopy data give clear evidences that no  $\text{MoS}_4^{2-}$  units are present in PX.

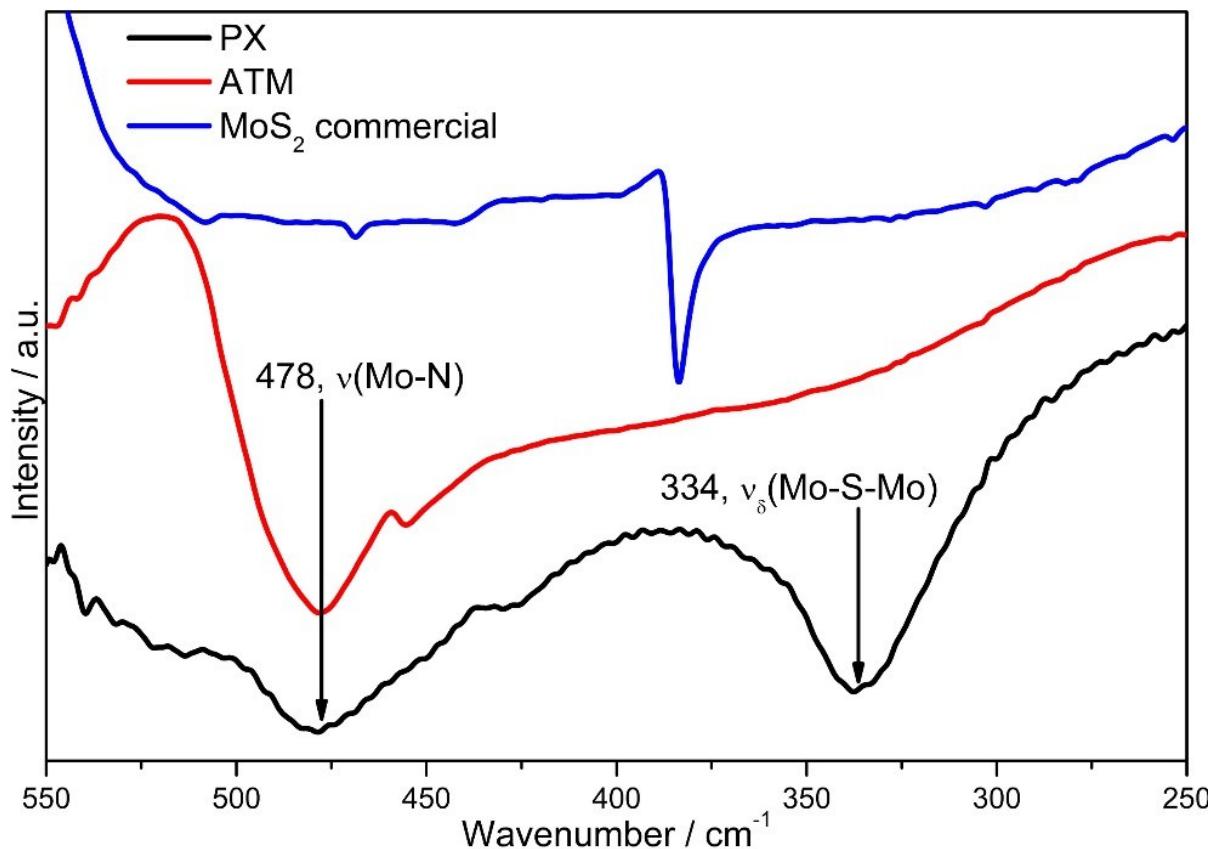
### 3. Far Infrared Measurements (FIR)

The FIR spectra (**Figure S3**) of PX heated to 450/900 °C and of commercial  $\text{MoS}_2$  display the signals of the  $\text{A}_{2u}$  (out-of-plane) and the  $\text{E}_{1u}$  (in-plane) vibrations of the planes of  $\text{MoS}_2$  at 468 and  $383 \text{ cm}^{-1}$ . The  $\text{A}_{2u}$  vibration exhibits a pronounced variation of the intensity. While commercial  $\text{MoS}_2$  only shows a weak  $\text{A}_{2u}$  band, those of the materials heated to 450 and 900 are more intense. The other band can be assigned to the in plane vibration of  $\text{MoS}_2$  which is present in all three samples - commercial  $\text{MoS}_2$ , PX450 and PX900 – with more or less the same intensities which does not depend on the number of stacked  $\text{MoS}_2$  layers. For the as prepared sample none of these absorptions can be seen in the spectrum, but two broad signals at about 480 and  $340 \text{ cm}^{-1}$ .



**Figure S3.** FIR of PX (black trace) in comparison with PX450 (green trace), PX900 (orange trace) and commercial  $\text{MoS}_2$  (light blue trace).

**Figure S4** again depicts the FIR of PX in comparison with ATM and commercial  $\text{MoS}_2$ . The absorption at  $480 \text{ cm}^{-1}$  may be caused by a Mo-H<sub>2</sub>O vibration ( $477 \text{ cm}^{-1}$ ) due to contamination with water from the air, but in this case two more bands at about  $511 \text{ cm}^{-1}$  and  $551 \text{ cm}^{-1}$  should be seen which are not present. The XPS measurements (see SI Figure S2) in the O 1s region give no hints for the presence of H<sub>2</sub>O. According to literature the signal can be assigned to the Mo-N vibration of a Mo-NH<sub>2</sub>-NH<sub>2</sub> coordination.<sup>1,2</sup> The second band at  $334 \text{ cm}^{-1}$  can be assigned to a bridging  $\text{S}_2\text{S}^{2-}$  ligand between two Mo atoms. This band was assigned to imperfections in the arrangement of  $\text{MoS}_2$  sheets which have defects in their basal sulphur atom arrangement or in other words interconnections of two layers by Mo-S-Mo bridges.<sup>3</sup>



**Figure S4.** FIR of PX (black trace) in comparison with ATM (red trace) and commercial bulk  $\text{MoS}_2$  (blue trace).

#### 4. X-ray photoemission spectroscopy (XPS)

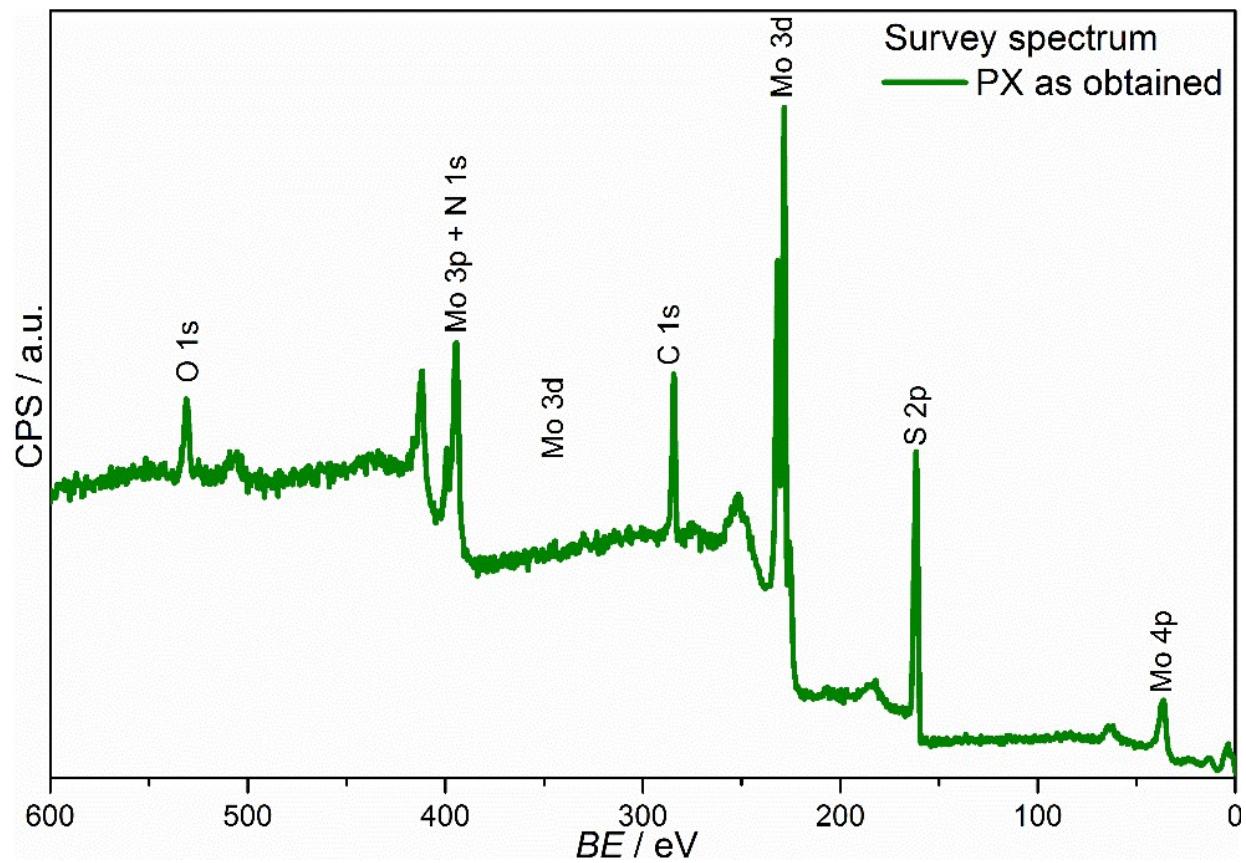
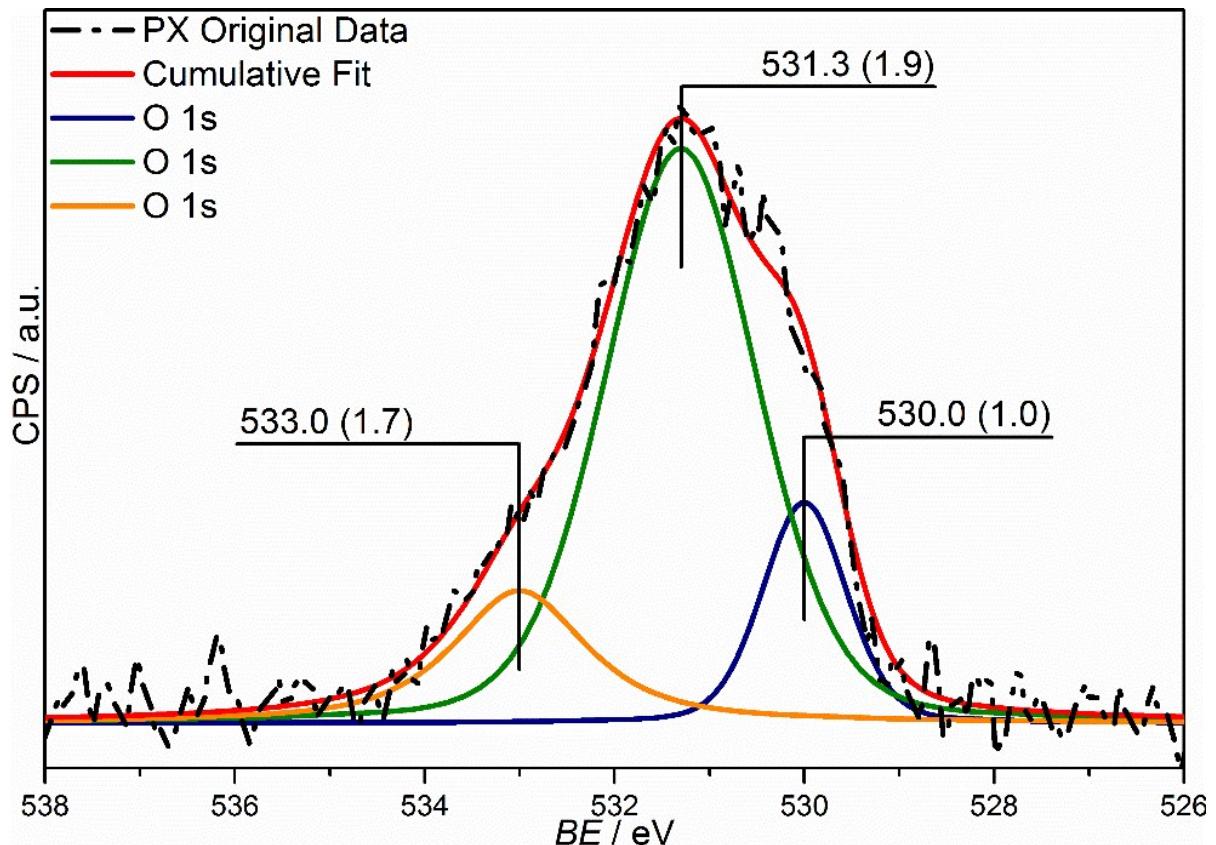
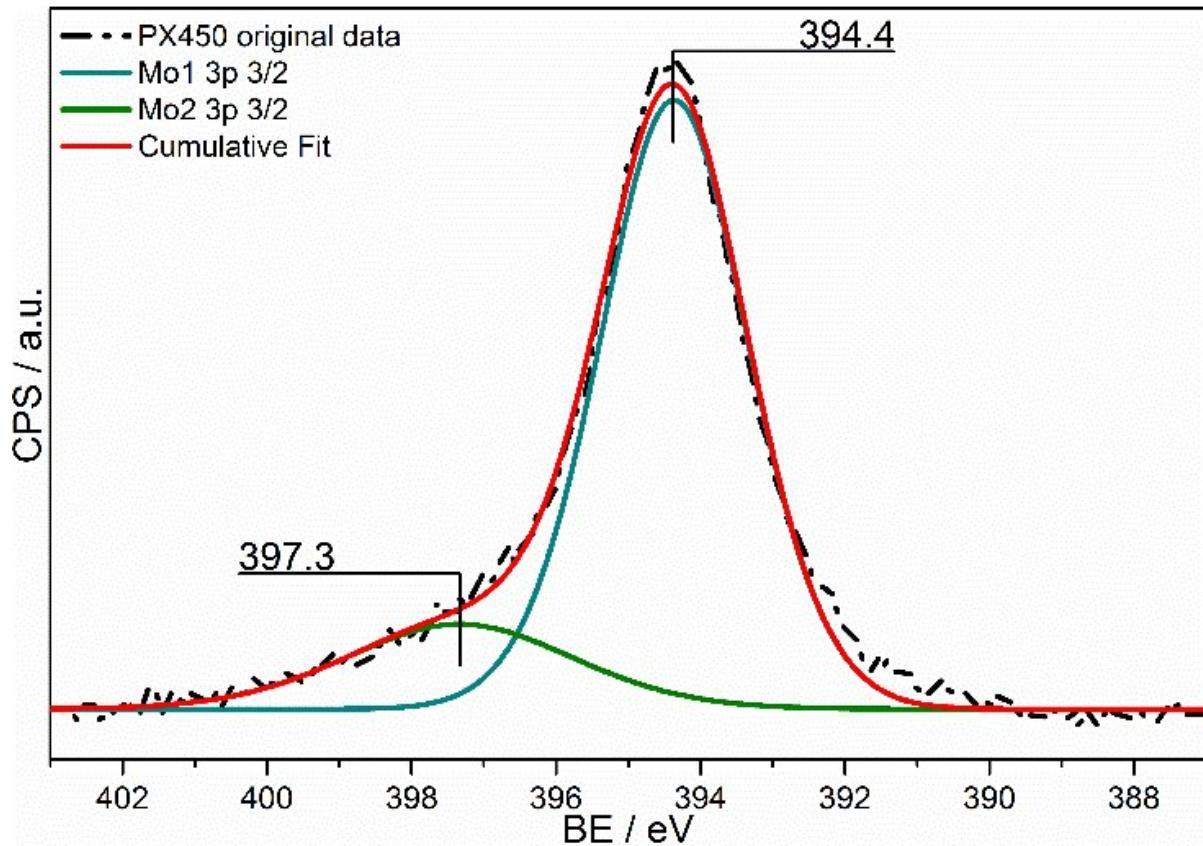


Figure S5. XPS survey spectrum of PX.

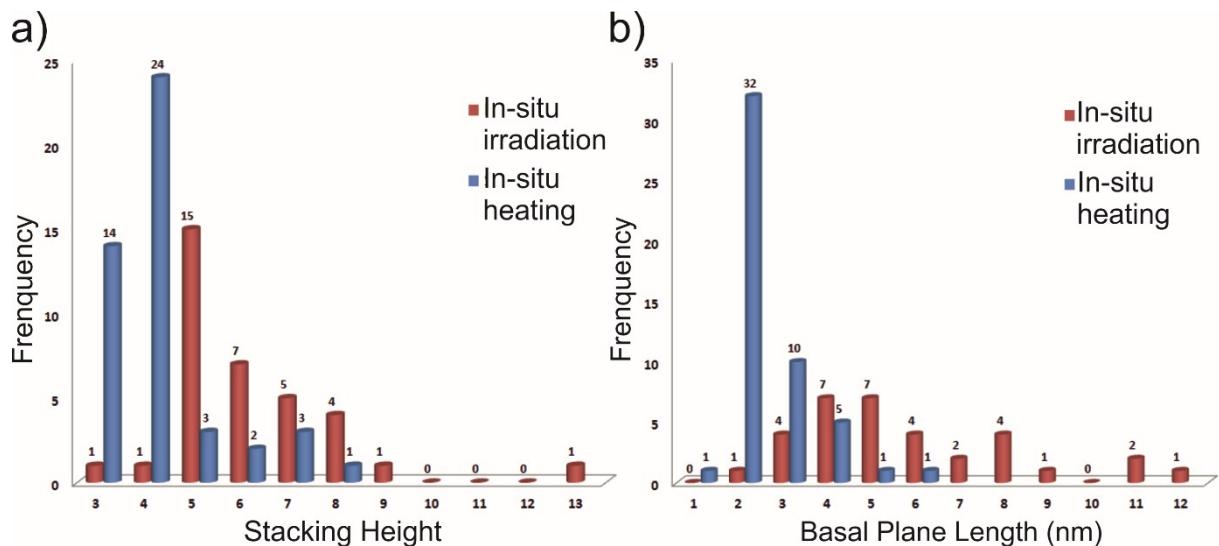


**Figure S6.** XPS measurement of the O 1s region of PX as obtained with the original data (black dash dotted trace), the cumulative fit (red trace) and the O 1s fitted curves (various colors).



**Figure S7.** XPS measurement of the N 1s region of PX after heating to 450 °C (PX450) with the original data (black dash dotted trace), the cumulative fit (red trace) and the Mo 2p<sub>3/2</sub> fitted curves (green and blue trace).

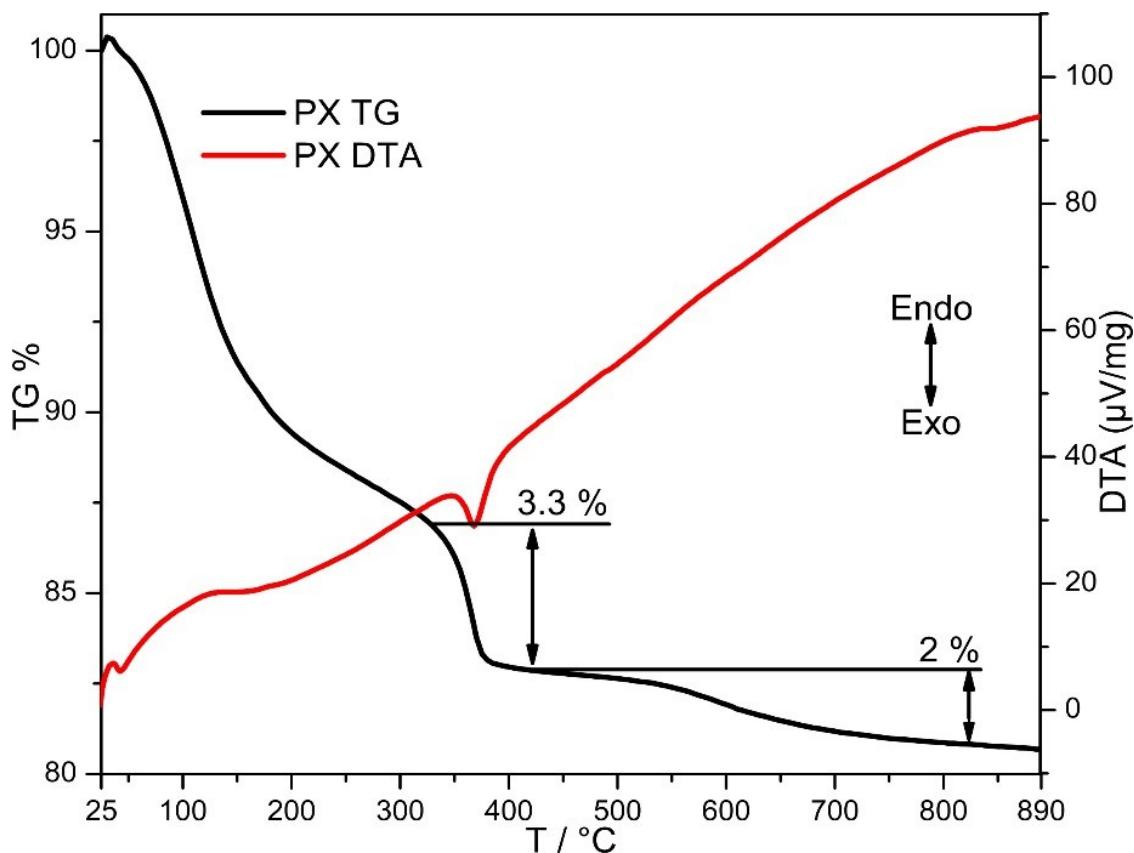
## 6. TEM analysis



**Figure S8.** (a) Stacking height distribution counted from the HRTEM micrograph where PX was under in-situ irradiation after 1 hour (red column), and from the micrograph where the sample was in-situ heated to 500 °C (blue column). (b) Basal plane length distribution of the in-situ irradiated (red column) and in-situ heated (blue column) PX sample.

## 7. Thermal analyses (DTA/TG)

The thermal decomposition reaction of PX was studied with DTA-TG up to 900 °C in inert atmosphere (heating rate: 4 K/min; **Figure S9**). The weight loss starts at relatively low temperatures and a not well resolved step occurs at about 350 °C. During this decomposition reaction several N containing species such as NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> are emitted from the sample (MS spectra not shown here). Above about 350 °C another mass loss of about 3.3 % is accompanied by an exothermic event in the DTA curve indicative for the onset of crystallization of MoS<sub>2</sub>. For the thermal decomposition of ATM it is proposed that MoS<sub>3</sub> forms as an intermediate material<sup>4,5</sup> followed by decomposition of MoS<sub>3</sub> and crystallization of MoS<sub>2</sub> which is also accompanied by an exothermic event. The XRD pattern of the compound heated to 450 °C (Fig. 2) shows the presence of highly disordered MoS<sub>2</sub> slabs supporting the assumption that the exothermic event is caused by the crystallization process. In the temperature range from 400 to 900 °C only a small weight loss of about 2 % occurs which may be due to the emission of material incorporated between the expanded van der Waals gaps (see discussion above). The formation of MoS<sub>2</sub> slabs also matches the XPS measurements of PX heated to 450 °C, where a new Mo species occurred with a binding energy matching with Mo in the oxidation state +IV while the two other species vanished.



**Figure S9.** Thermal analysis (DTA/TG) of PX up to 900 °C.

Another set of heating experiments has been conducted where the temperature has been raised successively to specific values and the respective samples were directly examined via elemental analyses (Table S1).

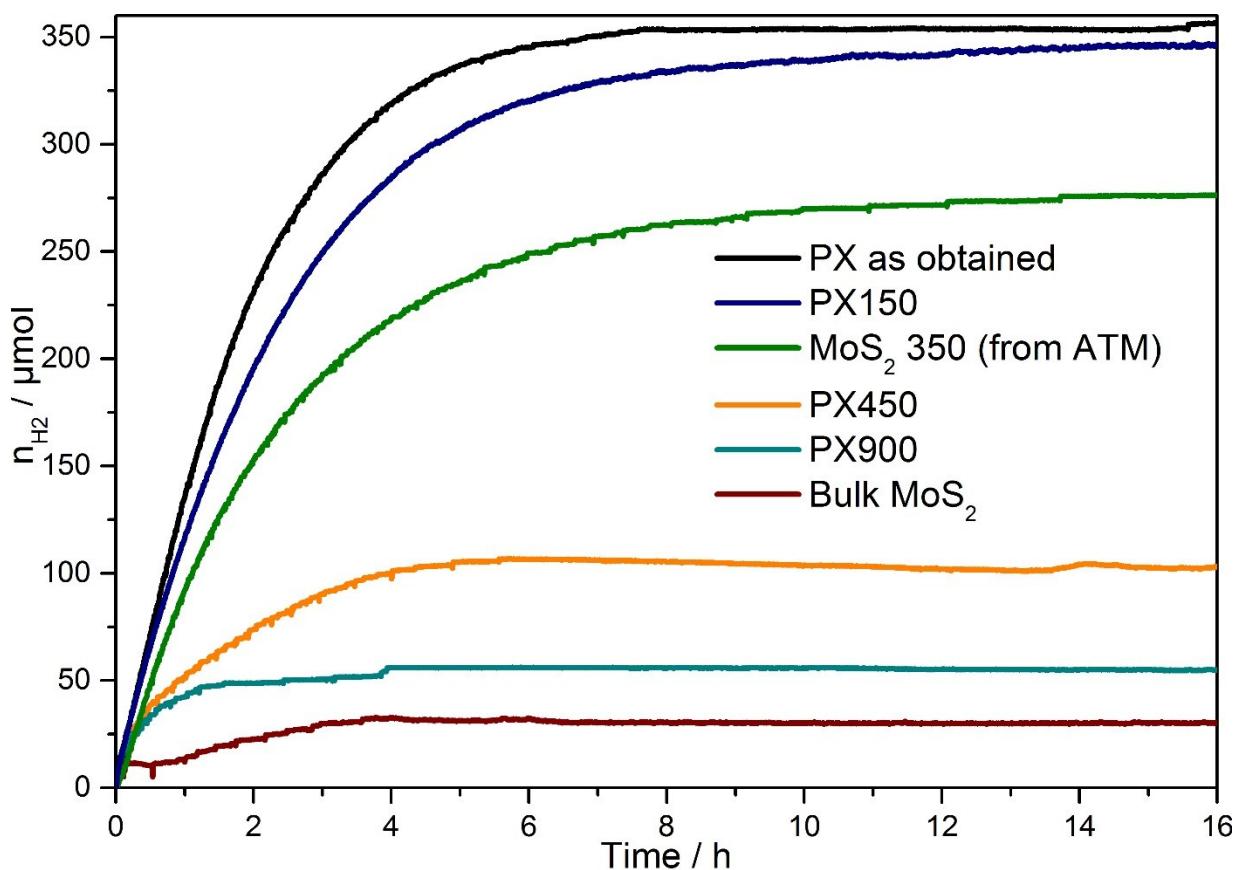
**Table S1.** Heating experiments of PX to various temperatures and results of the elemental analyses.

Sample	Heating temperature / °C	N %	H %	N : H molar ratio
PX	---	various	various	Between 1 : 4 and 1:5
PX100	100	4.95	1.41	1 : 4.0
PX200	200	4.01	0.95	1 : 3.3
PX300	300	2.98	0.51	1 : 2.4
PX340	340	2.03	0.31	1 : 2.2
PX350	350	1.98	0.28	1 : 2.0
PX360	360	1.50	0.16	1 : 1.4

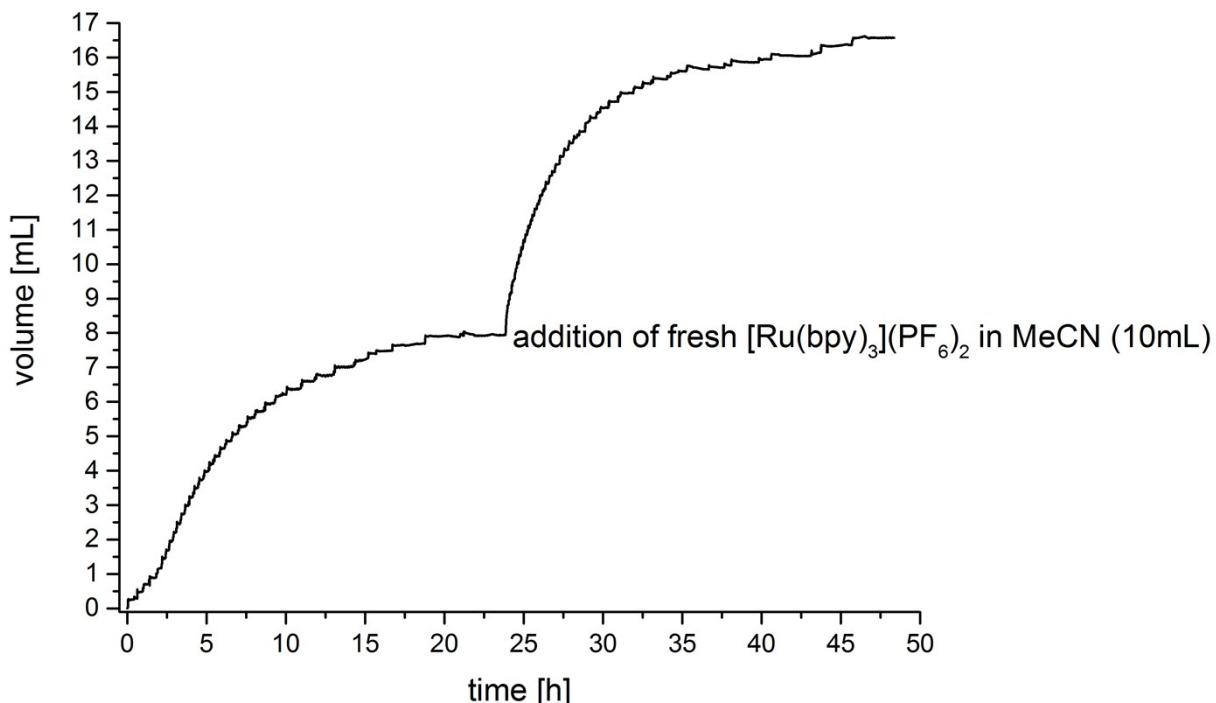
The as prepared PX contains ratios of N : H between 1 : 4 and 1 : 5. This depends on the sample as the nitrogen and hydrogen contents are varying. Upon heating the sample loses both N and

H, but H at a larger rate. Thus the molar ratio of N : H reaches 1 : 2.0 exactly at 350 °C, which is the temperature of crystallization. This ratio fits perfectly to hydrazine ( $N_2H_4$ ) and gives another hint that up to that crystallization hydrazine is involved in the material. Another  $NH_x$  species seems to be present in the as prepared compound as well but is emitted upon heating prior to hydrazine.

## 8. Visible-light driven hydrogen evolution



**Figure S10.** Development of the  $H_2$  production during 16 hours of irradiation of PX as obtained (black trace), three heated samples (150 °C dark blue trace, 450 °C orange trace, 900 °C light blue trace), commercial bulk MoS<sub>2</sub> (dark red trace), and nanocrystalline MoS<sub>2</sub> prepared via a thermal decomposition of ATM at 350 °C for comparison (green trace).



**Figure S11.** Depiction of a measurement of PX and the deactivation of the photosensitizer and addition of fresh PS to reinitialize the reaction.

The deactivation of the Ru dye leads to a retardation of the whole reaction. To proof that the photosensitizer is the weak component it was reapplied after the reaction had completely stopped after 25 h of reaction. After the PS was added, the system had time to equilibrate and then the reaction was reinitialized with light, which started the reaction immediately. This proofed that the catalyst is stable under the reaction conditions.

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