

## Supporting Information

### Chemistry of the photoisomerization and thermal reset of nitro-spiropyran and merocyanine molecules on the channel of the MoS<sub>2</sub> field effect transistor

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## 1. The optical contrast method for the flake thickness determination

It is possible to estimate the thickness of the MoS<sub>2</sub> layer by measuring the contrast of the reflected light from the SiO<sub>2</sub> surface with and without the presence of the MoS<sub>2</sub> flake.<sup>1</sup> The contrast is defined with the following equation:

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}$$

where  $R_0(\lambda)$  and  $R(\lambda)$  are the intensities of the reflected light without and with MoS<sub>2</sub> for the wavelength of  $\lambda$ , respectively. It was suggested that the use of  $\lambda$  in the red region is more efficient compare to the use of the blue and green lights.<sup>1</sup> For the device used in this report, the  $C(\lambda)$  of the red light was found to be 0.5, which indicates the number of the layers of the flake to be four from the table calibrated previously.<sup>1</sup>

## 2. Device fabrication process

The substrate (300 nm SiO<sub>2</sub>/p<sup>++</sup>Si) was cleaned by acetone and isopropanol separately through ultra-sonication bath for 5 min. Then it was dried by the N<sub>2</sub> gun and then the substrate was treated under UV-O<sub>3</sub> treatment for 30 min to remove any organic impurities. The MoS<sub>2</sub> flakes were transferred to substrate by the mechanically exfoliated technique. The flake was covered by the MMA (methyl methacrylate) and poly (methyl methacrylate) (PMMA A2) resist. Then electron beam lithography (ELS-700, ELIONIX) was carried out for making the electrode pattern. After developing by the developer solvent, Ti (10 nm) /Au (150 nm) source and drain contacts were formed by EB evaporator. Finally, lift-off was done through wet removal by N-methyl-2-pyrrolidone (NMP).

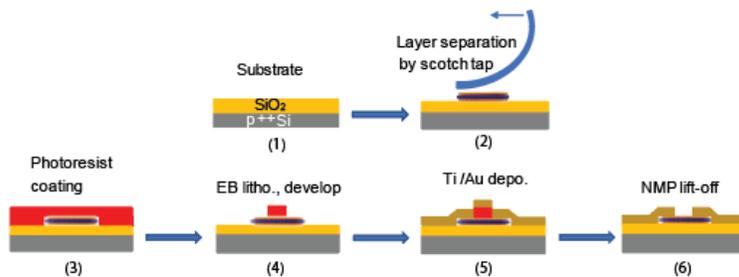


Figure S1. Device fabrication process for MoS<sub>2</sub>-FET.

### 3. Spiropyran coverage estimation on MoS<sub>2</sub> from XPS data

We estimated the coverage as the number of layers of the SP molecule by using the following 6 steps:

Step 1) Calculated the kinetic energy ( $E_k$ ) of N 1s and Mo 3d electrons.

Step 2) Calculated the mean free path ( $\lambda$ ) of N 1s and Mo 3d electrons.

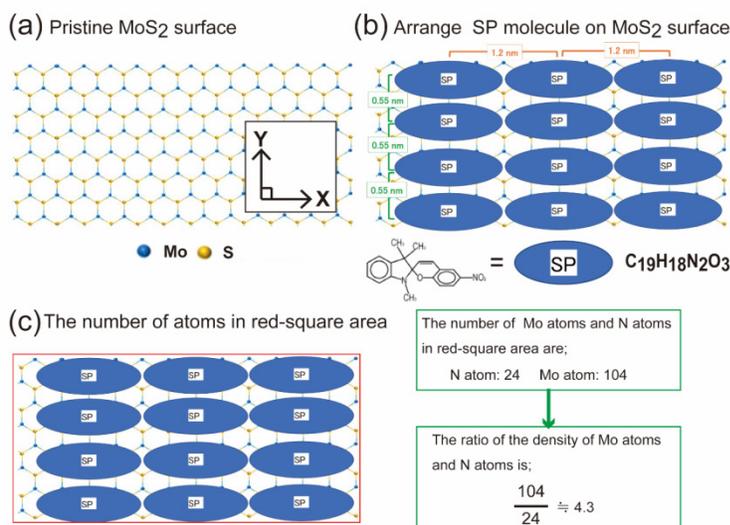
Step 3) Calibrate the pristine MoS<sub>2</sub> thickness, which was 4 layers.

Step 4) Estimate the ratio of areal densities of N and Mo atoms.

Step 5) Examine the signal intensities ratio between N 1s and Mo 3d as the function of the amount of the deposited SP molecule.

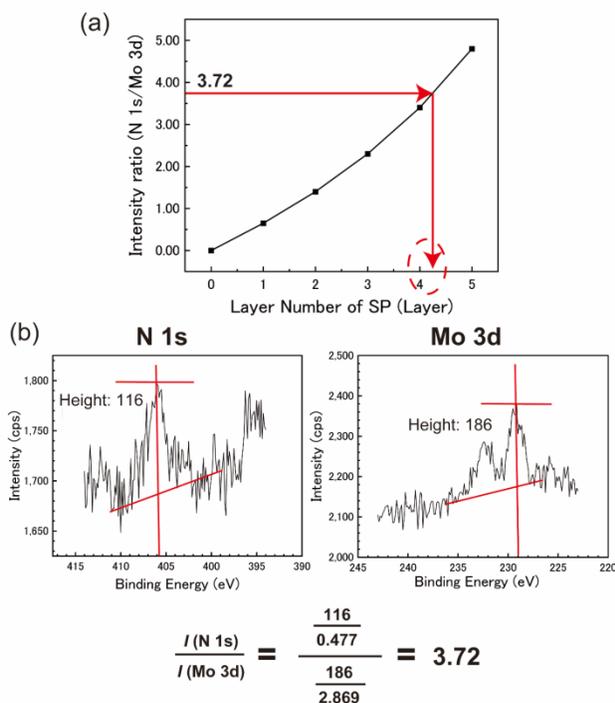
Step 6) Determine the thickness of SP layer.

The conversion of the amount of the SP molecule calculated from the ratio of step 4) is converted into the number of the SP layers based on the model shown in Figure S2, where the lattice of the SP molecule is taken from the data of previously reported STM data of TCNQ on Au surface. The actual XPS spectra, background subtraction and the calculation with the element coefficients are illustrated in Figure S3.



**Figure S2.** The model of the surface density ratio of Mo atoms to N atoms. (a) MoS<sub>2</sub> plane as a base was prepared. (b) With reference to the previously reported STM image<sup>4</sup>,

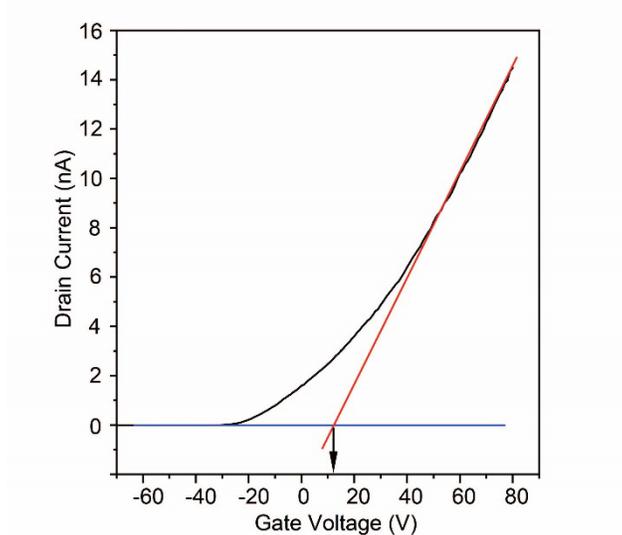
SPs were placed 1.2 nm in the X-axis direction and 0.55 nm in the Y-axis direction. In this model, the benzene ring of the molecule lays parallel to the MoS<sub>2</sub> surface. (c) In the plane of the red frame where the period of MoS<sub>2</sub> and the period of SP are almost the same, we counted the number of N atoms and Mo atoms, respectively. Since there were 24 N atoms and 104 Mo atoms, the areal density ratio of Mo atoms to N atoms was calculated to be ~ 4.3.



**Figure S3.** The estimation of SP thickness from XPS experiment. (a) The theoretical plot of “SP coverage (layer number)” vs “Intensity ratio of N atom (derived from SP) and Mo atom (derived from MoS<sub>2</sub>)”. (b) The XPS narrow spectra of N 1s (left) and Mo 3d (right), respectively.

#### 4. Threshold voltage determination

From the  $I_d$ - $V_g$  plot we obtain a characteristics  $I_{ds}$  which varies linearly with the  $V_g$  for a fixed  $V_d$ . The  $I_d$ - $V_g$  behavior in the linear regime is extrapolated to zero  $I_d$  and abscissa we obtain is a good evaluation of the threshold voltage ( $V_{th}$ )<sup>5</sup> shown in Figure S4.



**Figure S4.** Threshold voltage determination method for the pristine device.

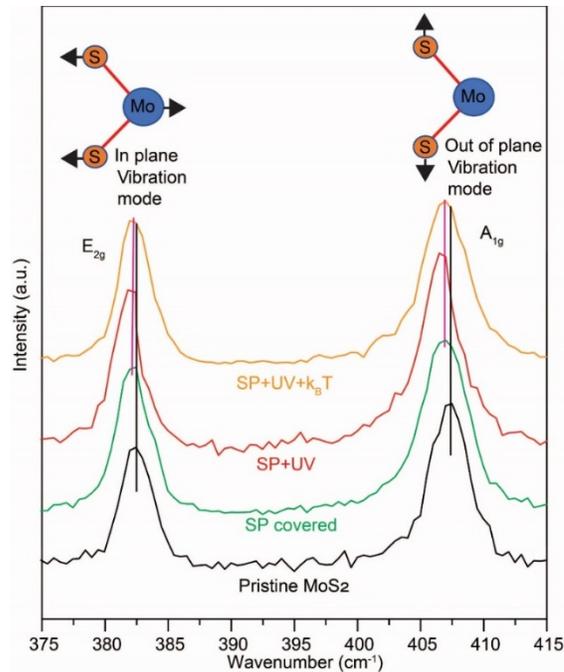
#### 5. Table for the rate constants with corresponding temperatures

The results of the fitting for the plots shown in Figure 4.

Table 1. Rate constants with corresponding temperatures.

Rate Constants ( $k$ )	$\ln k$	Temperature, T (K)	1/T
0.00069	-7.289	298.15	0.00335
0.00505	-5.289	313.15	0.00319
0.00879	-4.734	323.15	0.00309
0.02163	-3.833	333.15	0.00300
0.09066	-2.400	343.15	0.00291
0.22543	-1.489	353.15	0.00283

## 6. Raman spectroscopy analysis

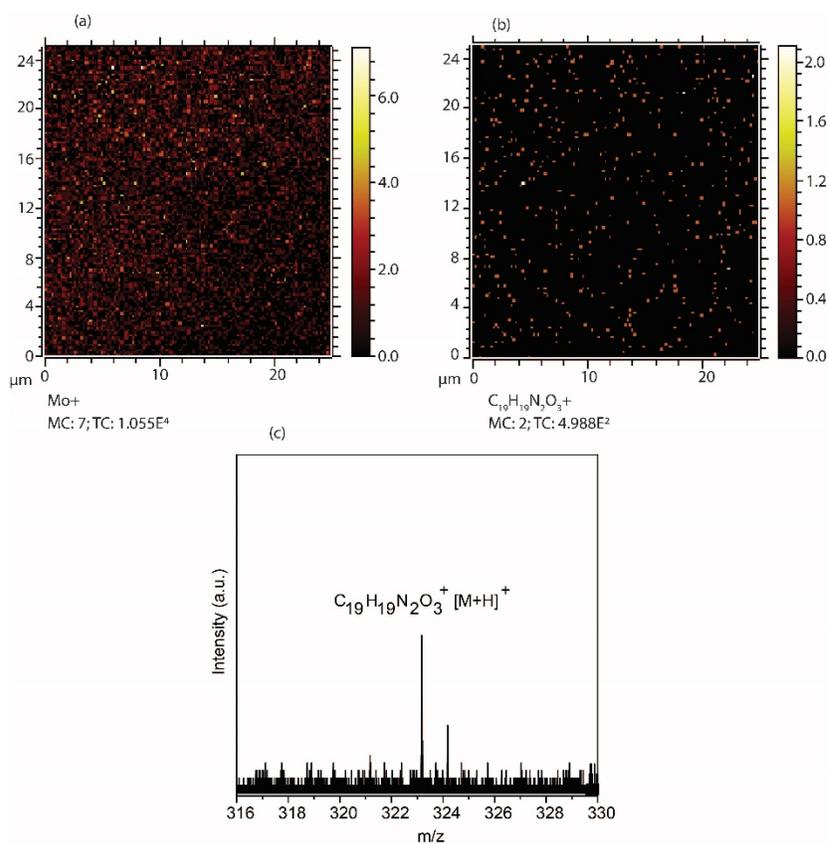


**Figure S5.** Raman peaks of pristine MoS<sub>2</sub>, after SP covered, after UV irradiation on SP surface and after heat treatment on MC.

Figure S5 shows the two characteristic peaks  $E_{2g}$  and  $A_{1g}$  of MoS<sub>2</sub>. After SP deposition,  $E_{2g}$  and  $A_{1g}$  peaks shifted to the left side indicates the n-doping of MoS<sub>2</sub> by SP molecules. After UV irradiation on SP covered surface, both peaks shifted more left side which tells that MC also acting as n dopants for the MoS<sub>2</sub>. To recover the former SP molecules device was heated at around 80° C for 3 min thus makes the MC to SP again. This thermal conversion of MC to SP is visible in the Raman spectrum in which the  $E_{2g}$  and  $A_{1g}$  peaks come back the SP position.

## 7. Time of Flight Secondary Ionization Mass Spectroscopy Analysis

To further confirm the adsorption configuration of SP, the time-of-flight secondary ionization mass spectroscopy (SIMS) was measured. Figure S6a and b represent the elemental mapping image showing the presence of  $\text{Mo}^+$  and  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2^+$  ions, respectively. The amplitude of the color scale corresponds to the maximum number of counts. TOF-SIMS confirms the presence of SP over the  $\text{MoS}_2$  surface as a  $[\text{M} + \text{H}]^+$  at 323.36 m/z, as shown in Figure S6c.



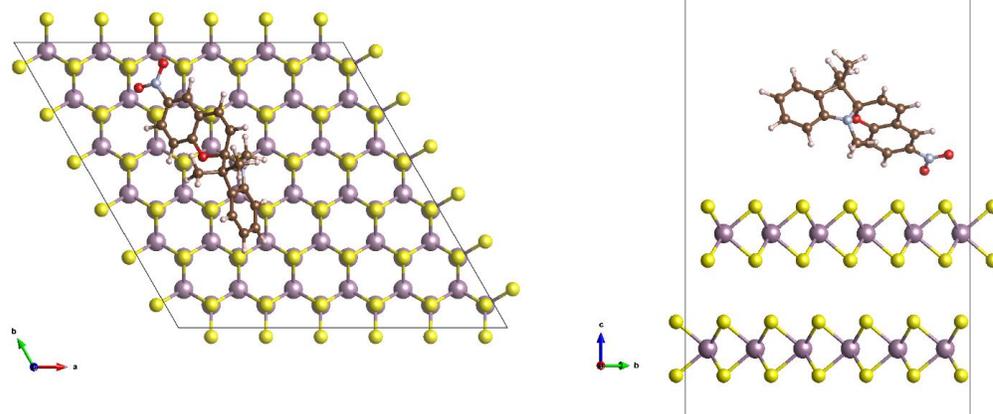
**Figure S6.** (a),(b) TOF-SIMS elemental mapping of  $\text{Mo}^+$  and  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2^+$ , respectively; (c) TOF-SIMS spectrum showing the  $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2^+$  peak as  $[\text{M}+\text{H}]$

## 8 Optimized adsorption configurations of Spiropyran and Merocyanine on MoS<sub>2</sub>

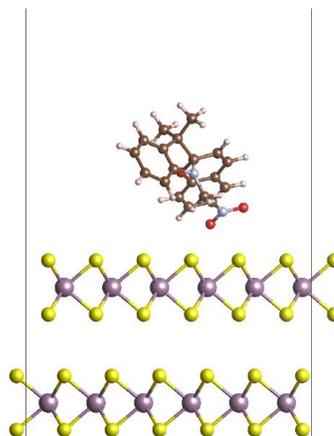
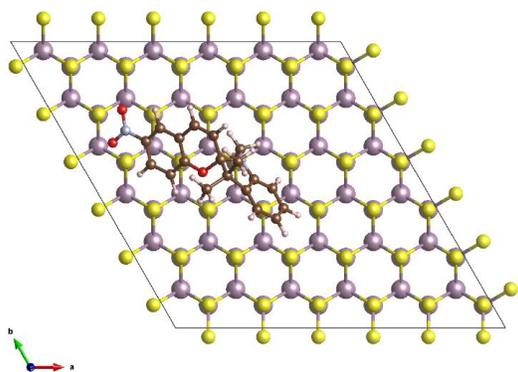
The optimized adsorption configuration for SP and MC molecules after the structural optimization starting from various initial configurations, which are plausible for the adsorption. Thus, they are representing the local minimum structures. For the SP molecule, two large group are considered; group A is the two apex of the bent configuration of SP are both attached to the substrate, and group B is that one of the two perimeters of the V shape molecule is adsorbed on the substrate in a flat-lying manner. For MC, the tilted-configuration of basically flat molecule structures is calculated to have the most stable configuration. Several models for each (total 21 models) were calculated and shown in Figure S7.

In addition, the calculated total energies for the models are shown in Table S2. We see the SP molecules give stable configurations than the MC molecules. The most stable model is SP-MoS<sub>2</sub>-B3 which is shown in the main text.

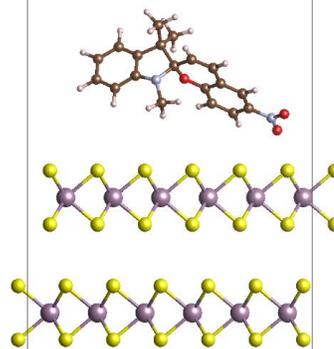
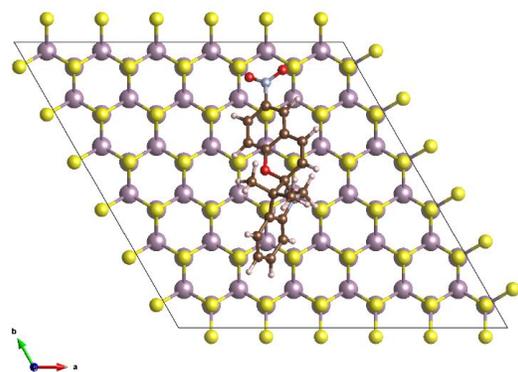
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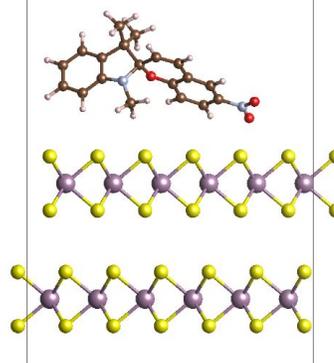
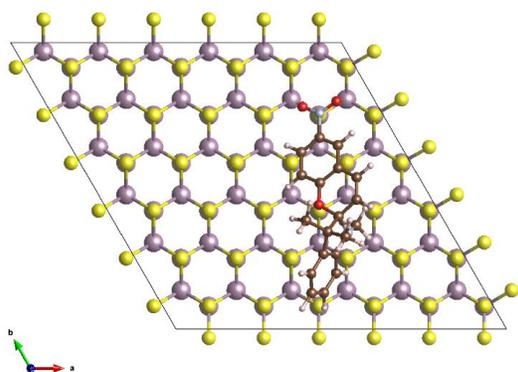
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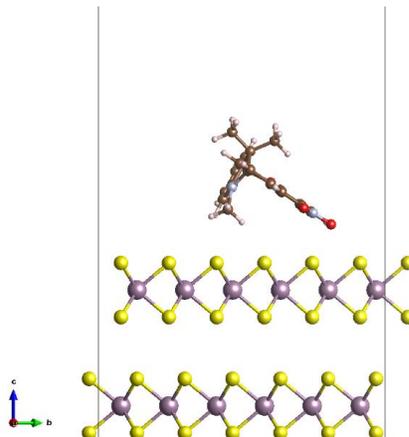
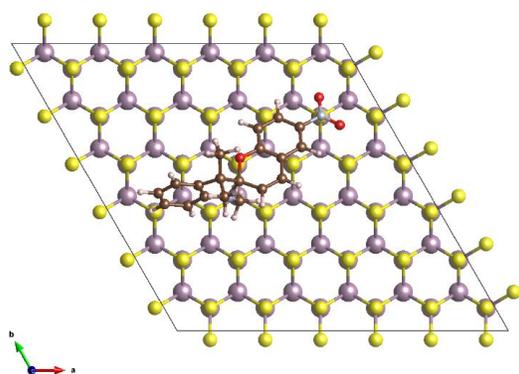
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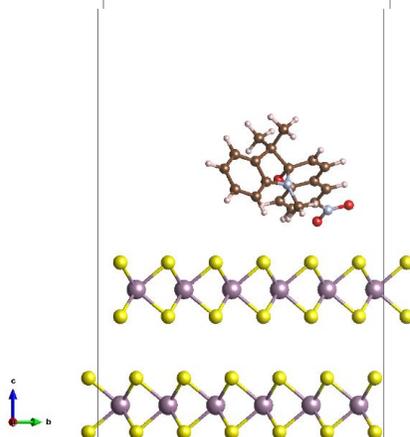
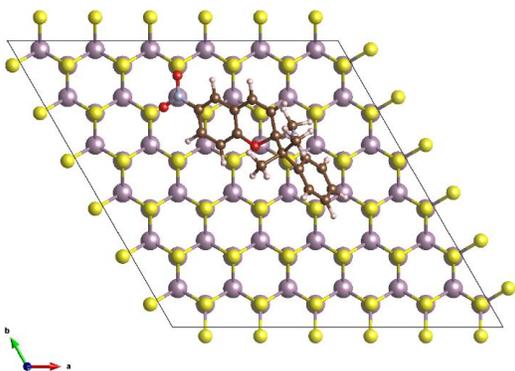
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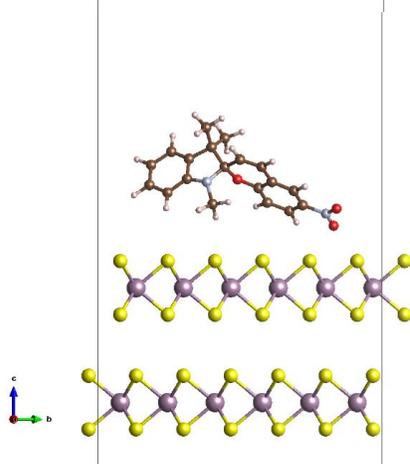
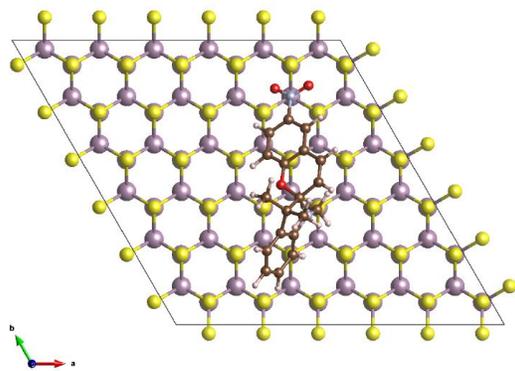
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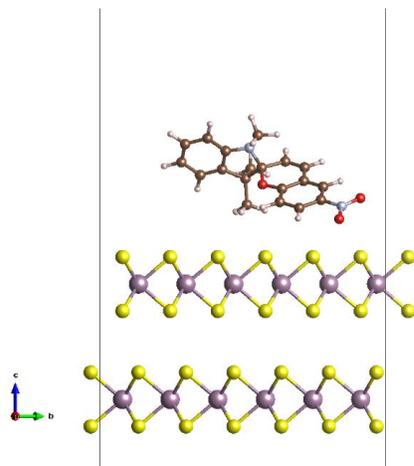
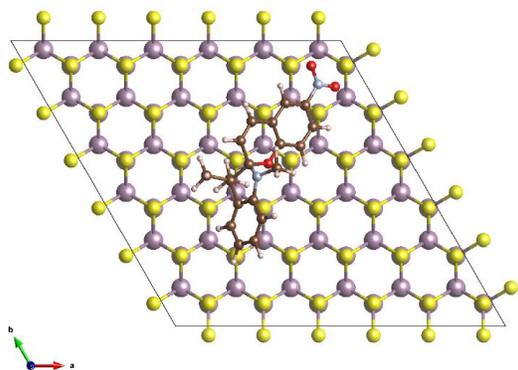
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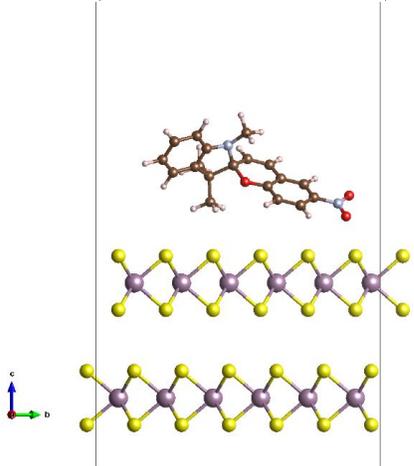
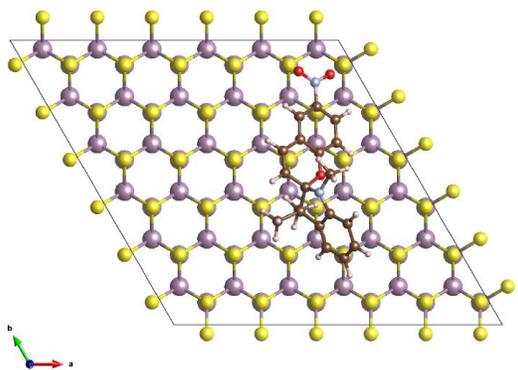
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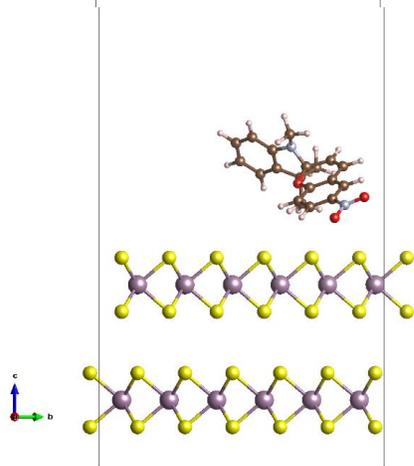
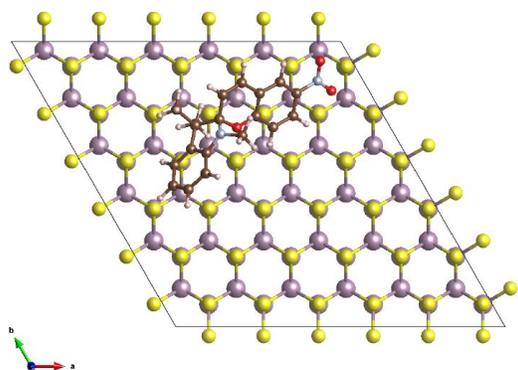
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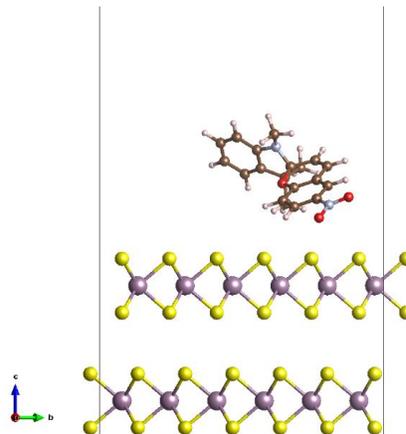
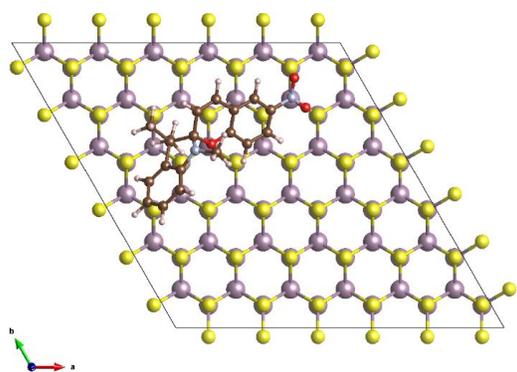
SP\_MoS2\_B\_2



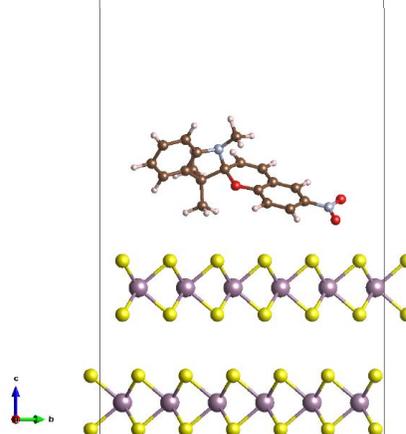
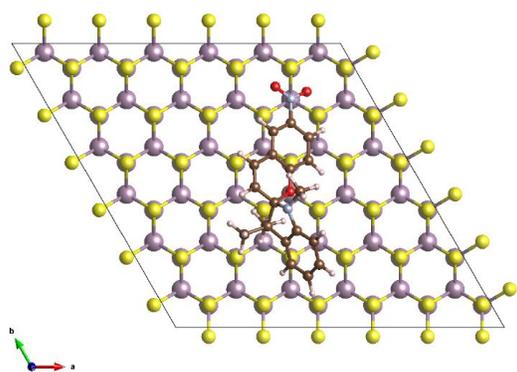
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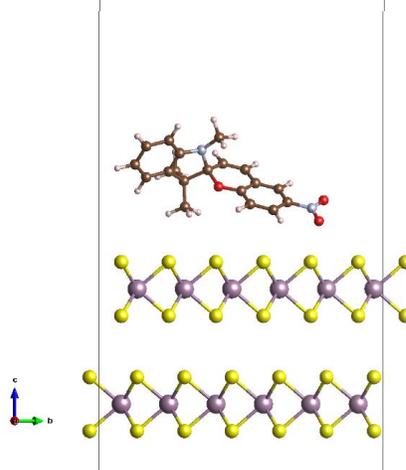
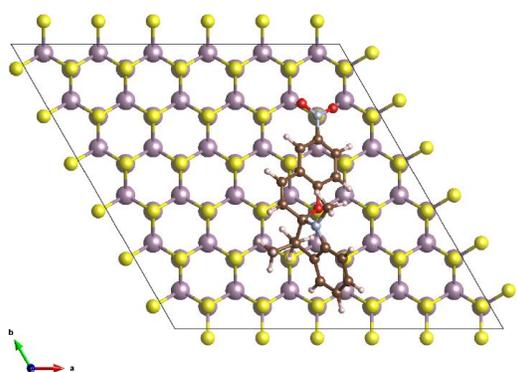
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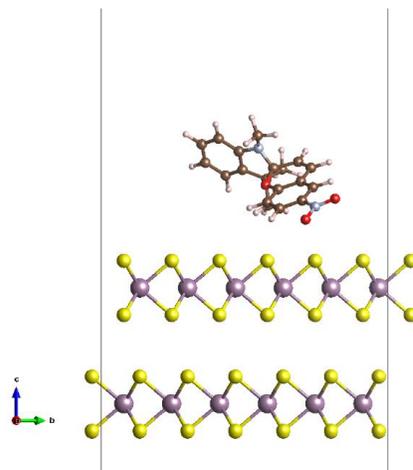
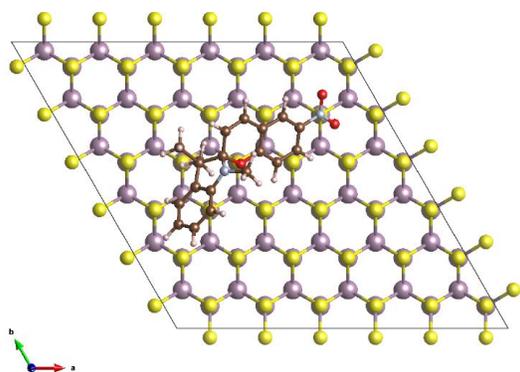
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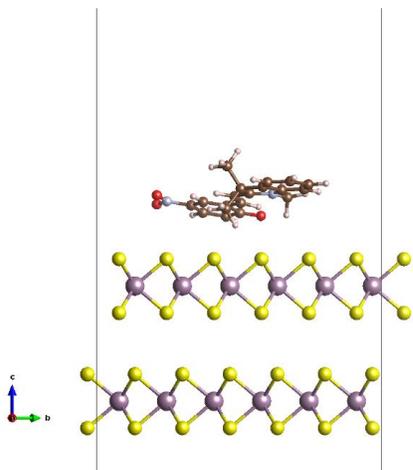
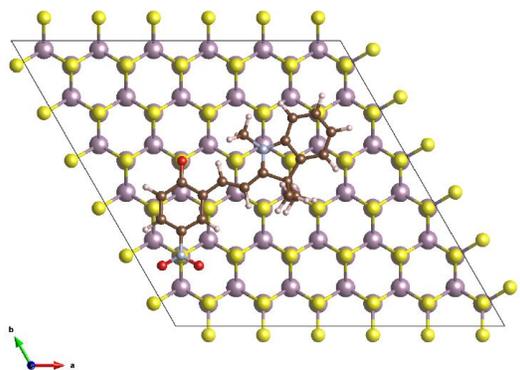
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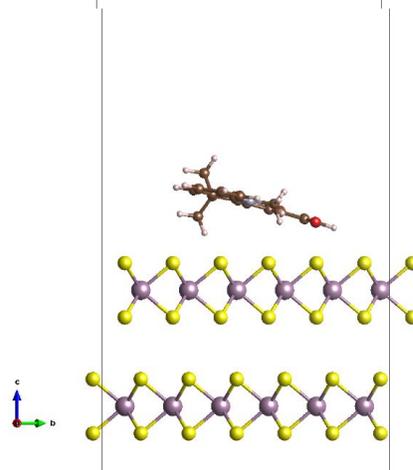
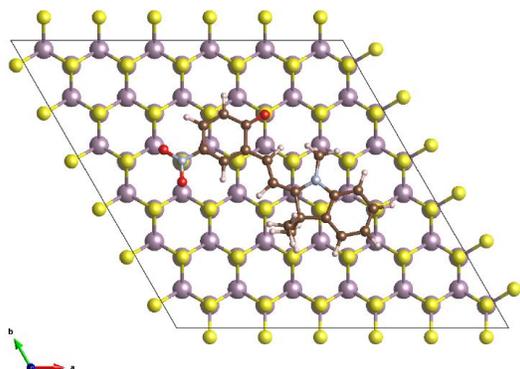
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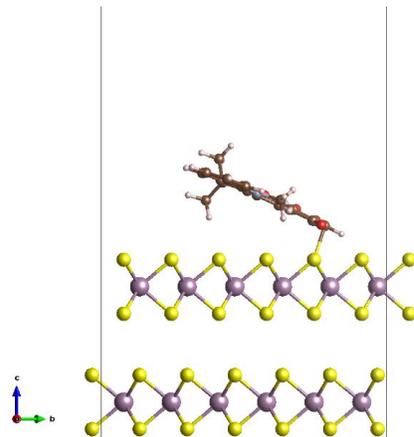
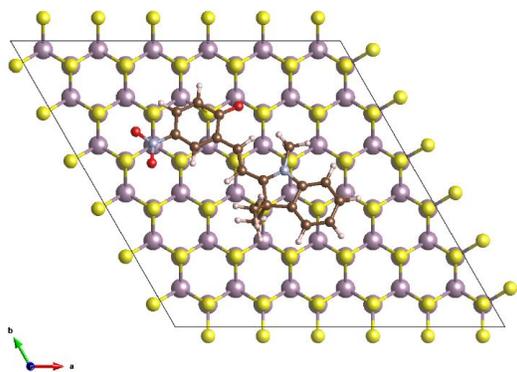
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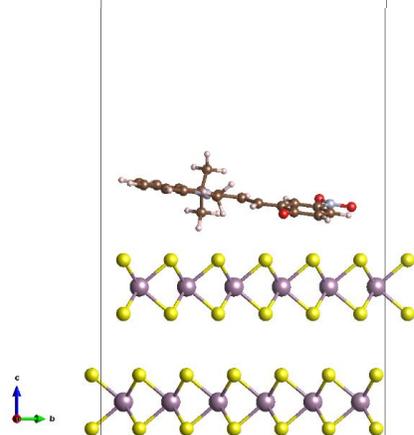
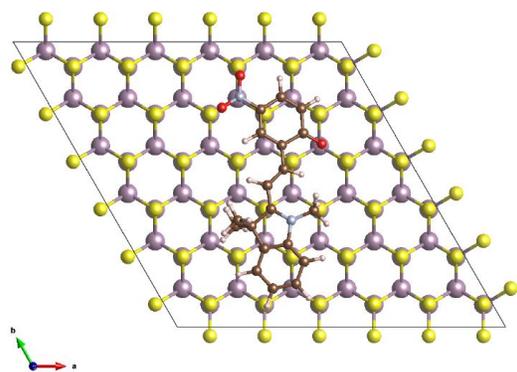
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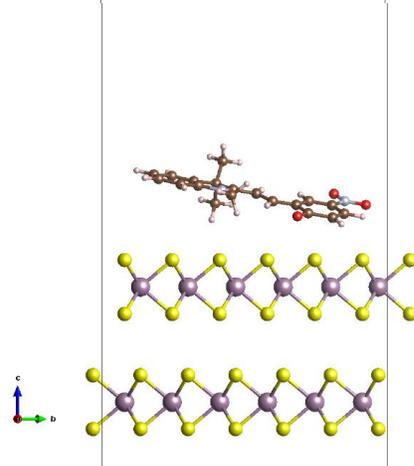
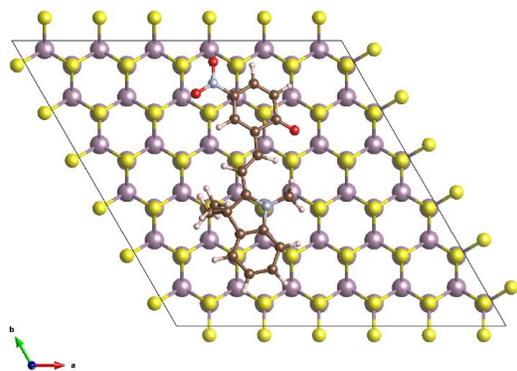
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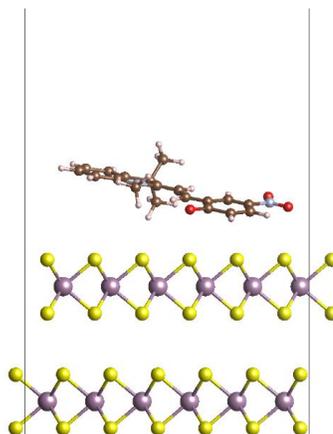
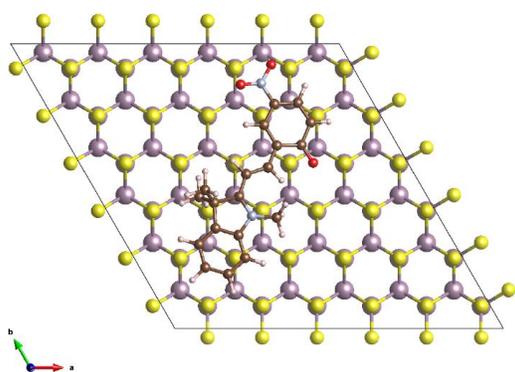
MC\_MoS2\_4



MC\_MoS2\_5



MC\_MoS2\_6



MC\_MoS2\_7

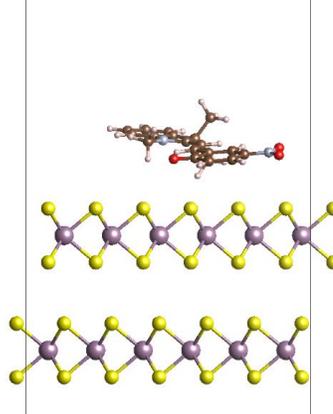
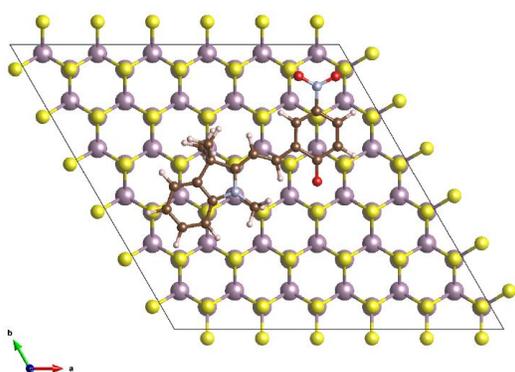


Figure S7. Optimized structures of of the SP and MC molecules adsorbed on MoS<sub>2</sub> surface. The calculation was started from various plausible configurations and the results of the strcutural optimization by VASP for the local minimum are illustrated.

Table S2. The total energies of the models of Figure S7. The most stable configuration is SP-MoS2-B3 which is shown with a bold font. For the MC molecule, the model of MC\_MoS2\_6 gives the lowest energy.

	Total energy (eV)
MC_MoS2_1	-3535.539
MC_MoS2_2	-3535.5134
MC_MoS2_3	-3535.5354
MC_MoS2_4	-3535.4873
MC_MoS2_5	-3535.5161
MC_MoS2_6	-3535.5711
MC_MoS2_7	-3535.4923
SP_MoS2_A_1	-3535.5693
SP_MoS2_A_2	-3535.5264
SP_MoS2_A_3	-3535.5441
SP_MoS2_A_4	-3535.5702
SP_MoS2_A_5	-3535.5171
SP_MoS2_A_6	-3535.5493
SP_MoS2_A_7	-3535.5674
SP_MoS2_B_1	-3535.4933
SP_MoS2_B_2	-3535.5386
<b>SP_MoS2_B_3</b>	<b>-3535.6159</b>
SP_MoS2_B_4	-3535.5654
SP_MoS2_B_5	-3535.4291
SP_MoS2_B_6	-3535.5037

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