

Supporting Information

A direct Fe-O coordination at FePc/MoO_x interface investigated by XPS and NEXAFS spectroscopies

Lingyun Liu^a, Wenhua Zhang^{a*}, Panpan Guo^a, Kai Wang^a, Jiaou Wang^b, Haijie Qian^b, Ibrahim
Kurash^b, Chia-Hsin Wang^c, Yaw-Wen Yang^c, and Faqiang Xu^{a*}

^a*National Synchrotron Radiation Laboratory, University of Science and Technology of China,
Hefei, Anhui 230029, P.R.China*

^b*Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of
Sciences, Beijing 100039, P.R.China*

^c*National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan*

* W. Zhang: email: zhaowh@ustc.edu.cn; tel, 86-551-63602060.

* F. Xu: email: fqxu@ustc.edu.cn; tel, 86-551-63602127.

1. Fitting parameters for Mo 3d

Table S1 shows Mo 3d XPS peak fitting parameters for Fig 1a of the manuscript, including binding energy (E_B), peak intensity (Intensity), and full width at half maximum (FWHM).

Mo species		E_B (eV)	Intensity	FWHM (eV)	Amount
As-depo	+6	3d _{3/2}	235.7	115	100%
		3d _{5/2}	232.6	220	
250 °C	+6	3d _{3/2}	235.7	98	51.1%
		3d _{5/2}	232.6	163	
	+m	3d _{3/2}	234.7	87	48.9%
		3d _{5/2}	231.6	163	
300 °C	+6	3d _{3/2}	235.7	165	61.2%
		3d _{5/2}	232.6	252	
	+m	3d _{3/2}	234.7	95	36.0%
		3d _{5/2}	231.6	150	
	+4	3d _{3/2}	232.2	8	2.8%
		3d _{5/2}	229.1	11	
350 °C	+6	3d _{3/2}	235.7	190	51.9%
		3d _{5/2}	232.6	310	
	+m	3d _{3/2}	234.7	106	26.6%
		3d _{5/2}	231.5	150	
	+n	3d _{3/2}	233.9	40	11.4%
		3d _{5/2}	230.6	70	
	+4	3d _{3/2}	232.2	39	10.1%
		3d _{5/2}	229.1	58	
400 °C	+6	3d _{3/2}	235.5	150	43.7%
		3d _{5/2}	232.6	208	
	+m	3d _{3/2}	234.6	65	20.8%

		3d _{5/2}	231.5	105	1.20	15.9%
		3d _{3/2}	233.7	50	1.20	
		3d _{5/2}	230.5	80	1.20	
	+4	3d _{3/2}	232.2	70	0.50	19.5%
		3d _{5/2}	229.1	90	0.55	
	450 °C	+6	3d _{3/2}	235.7	95	1.30
3d _{5/2}			232.6	173	1.30	
+m		3d _{3/2}	234.7	48	1.30	20.4%
		3d _{5/2}	231.5	76	1.25	
+n		3d _{3/2}	233.8	39	1.20	16.6%
		3d _{5/2}	230.5	62	1.25	
+4		3d _{3/2}	232.3	46	0.6	19.2%
		3d _{5/2}	229.2	71	0.6	

Note: “+m” and “+n” represent the medium states of Mo ions between +6 and +4 valence states. The Lorentz-Gaussian (GL%) ratio is fixed as 20% during the fitting process.

2. AFM image for MoO_x adsorbed with 1 ML FePc

Fig. S1 displays the morphology of 1 ML FePc adsorbed MoO_x sample. It is seen the FePc adsorption has less influence to the morphology of the MoO_x substrate after annealing at 400 °C. The MoO_x particles appear to be comparable to the size of the bare MoO_x substrate that shown in Figure 2b in the article. For the annealed FePc/MoO_x sample, the root mean square roughness is ~5.36 nm in contrast to the 1.2 nm of the bare MoO_x due to the FePc adsorption.

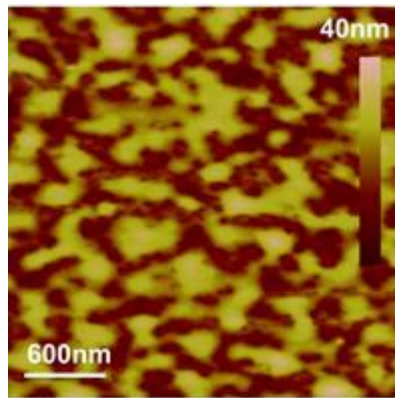


Fig. S1 The AFM image of FePc film adsorbed on the MoO_x surface annealed at 400 °C

3. N 1s core level

Figure S2 shows the N 1s XPS spectra for the multilayer (top) and monolayer (bottom) FePc films adsorbed on MoO_x. For the multilayer FePc films, the dominant peak at 398.6 eV are assigned to the two types of N atoms of the pyrrole (N_P) and the bridge nitrogen between the pyrrole ring (N_B). These two types of N atoms are difficult to resolve because of a small energy difference of ~0.2 eV. In addition, a small shoulder appears at the higher binding energy in both spectra, which are ascribed to the shake-ups of nitrogen. As to the one monolayer FePc, there is only one main peak at 399.6 eV, while a small shoulder can still be deconvoluted with a sharply declined intensity. There is a large energetic shift of about 1 eV between the one monolayer FePc and the multilayer FePc.

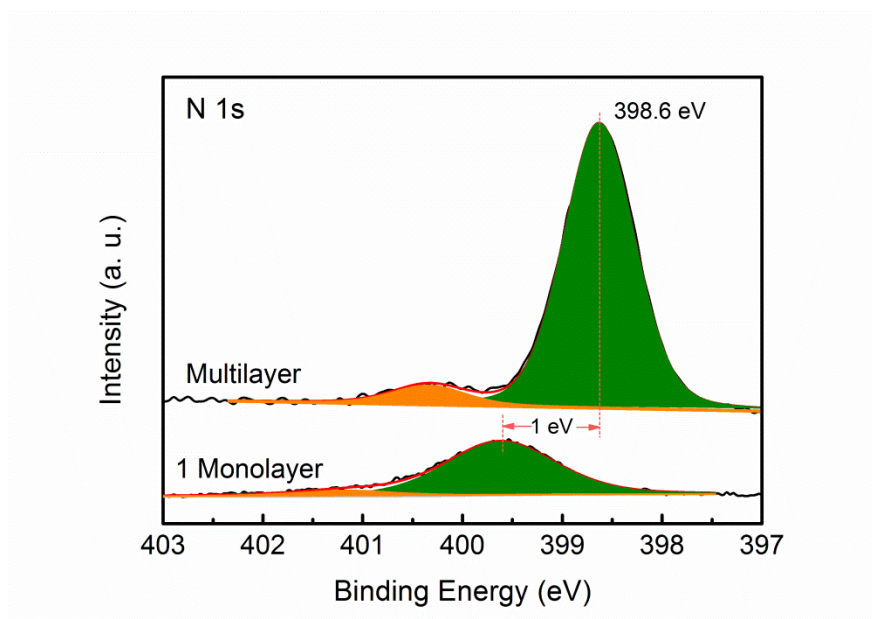


Figure S2 N 1s XPS spectra of the multilayer (top) and monolayer (bottom) FePc films adsorbed on MoO_x.

4. Fitting parameters for O 1s core level

Table S2 shows the fitting parameters and results for O 1s XPS spectra in Fig. 5 of the manuscript.

O 1s species		E _B (eV)	Intensity	FWHM (eV)	Amount
MoO_x	O-Mo ⁶⁺	530.2	81000	1.10	42.4%
	O-Mo ^{m,n+}	530.8	69042	1.25	36.1%
	O-Mo ⁴⁺	531.6	41000	1.50	21.5%
1 ML FePc/ MoO_x	O-Mo ⁶⁺	530.2	20000	1.00	19.0%
	O-Mo ^{m,n+}	530.7	50500	1.30	48.0%
	O-Mo ⁴⁺	531.6	25000	1.45	33.8%
	O _{new}	532.3	9600	1.31	9.2%

Note: “+m” and “+n” represent the oxygen species bonding to the Mo ions with +m and +n valence states, respectively. The two types of O-Mo bonds were fitted with one oxygen component due to the limited resolution. The Lorentz-Gaussian (GL%) is fixed as 20% during the fitting process.

5. C K-edge XAS spectra

Fig. S3 shows the dependence of C K-edge XAS spectra on the x-ray incidence angle (35° , 50° and 90°) for 1 ML FePc films adsorbed on the MoO_x substrate. The XAS spectra are characterized by multiple absorption peaks, basically associated with transitions to the empty states located on the benzene and pyrrole macrocycles of π^* and σ^* characters. It is seen the angular dependence of C K-edge is very small, suggesting a lack of uniform orientation in the film.

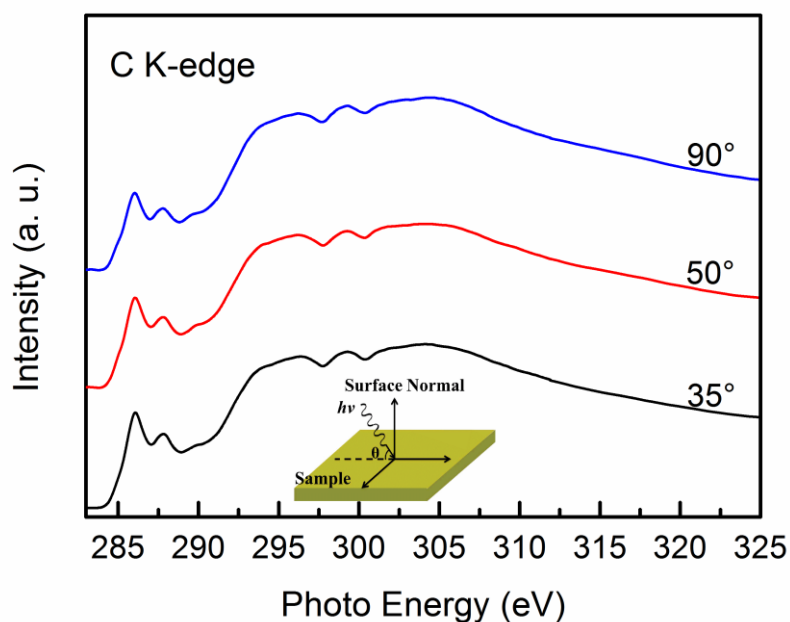


Fig. S3 C K-edge XAS spectra for 1 ML FePc film at different x-ray incidence angle of 35° , 50° and 90° . The inset shows the incident angle θ of the incident light with respect to the sample plane.

6. Fe 2p XPS spectra

Fig. S4 shows the Fe 2p XPS spectra for the 1 ML and multilayer FePc films that adsorbed on the MoO_x. Both spectra are dominated by two main peaks. The one at the BE of 721.8 eV is related to the Fe 2p_{1/2} level, and the other at BE of 708.4 eV is the 2p_{3/2} level. The Fe 2p of the 1 ML FePc sample shift ~0.7 eV towards the higher BE with respect to the multilayer.

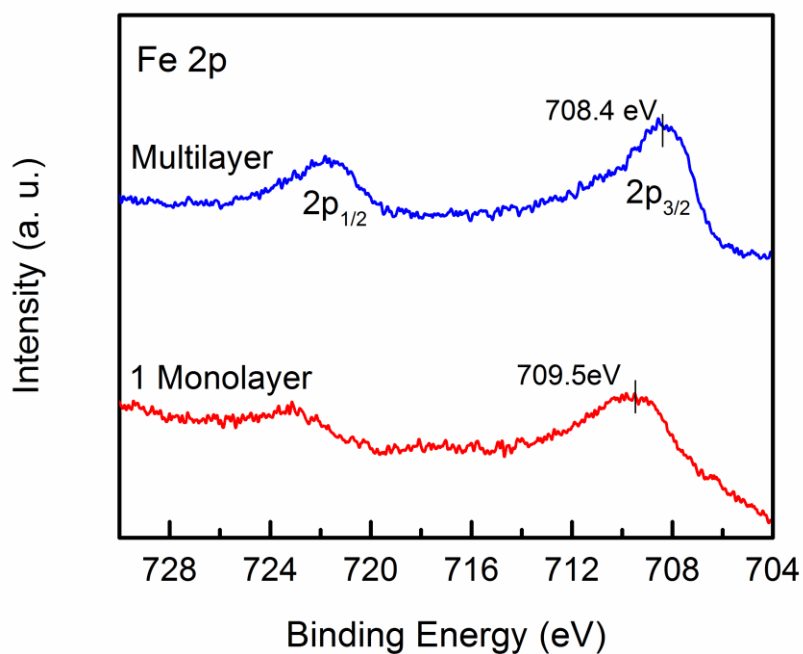


Figure S4 Fe 2p XPS spectra of the multilayer (top) and monolayer (bottom) FePc films adsorbed on MoO_x.