Supporting Information for

In-Situ Photoelectron Spectroscopy Investigation of Sulfurization-Induced Sodiophilic Sites with Model Systems of α-sexithiophene and p-sexiphenyl

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This Supplementary Material includes:

Na wettability tests of Cu, 6P-Cu and 6T-Cu; in-situ UPS spectra for sequential 6T deposition on silicon substrates; thickness and surface morphology of 6T and 6P films characterized by AFM; XPS spectra of Na 1s in different experiments: Na on 6T, 6T on Na, Na on 6P, and 6P on Na; detailed XPS peak fitting parameters for 6T with increasing Na deposition and Na with increasing 6T deposition.

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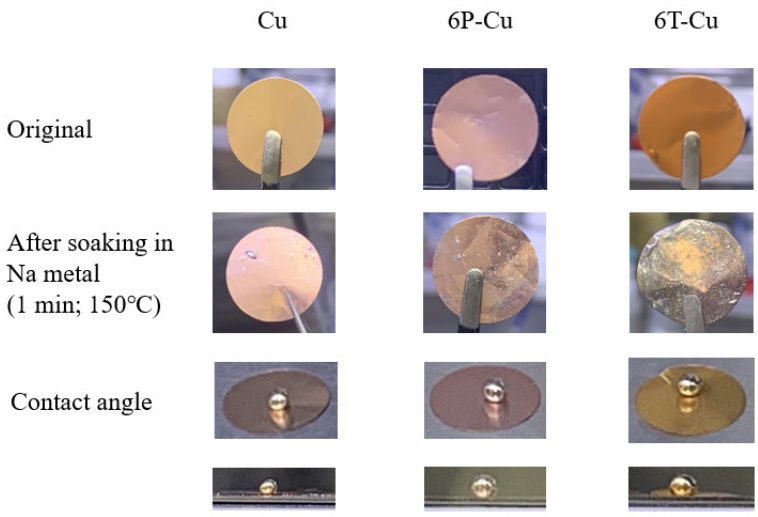

Figure S1. Na wettability tests of Cu, 6P-Cu, and 6T-Cu.

Na wettability tests were conducted to study the improved practical performance of different coatings. Through a resistively heating evaporator, 6P coating was applied on Cu foils at 230 ℃ for 30 minutes, and 6T coating was applied on Cu foils at 175 ℃ for 20 minutes. After preparation, they were soaked in molten sodium metal at 150 ℃ for 1 minute. It is found that nearly no Na is attached on the bare Cu sample, indicating weak Na wettability of Cu. For 6P-Cu, a small amount of Na is attached, and a larger amount of Na is attached on 6T-Cu, indicating improved Na wettability. It is also noticed that the interaction between Na and 6T is strong and nearly all 6T reacted with the sample making the color change. Moreover, the contact angles of these samples were tested with the molten sodium metal dropped on them, and the tested contact angles were shown to be similar with different coatings. However, for 6T coating samples, when the sodium ball is moved away, the color change at the contacting site can be observed, indicating a strong interaction between 6T and Na. For the similar contact angle, it can be explained that Na metal can hardly diffuse into the neighboring molecules around the contact site, thus showing a large contact angle.

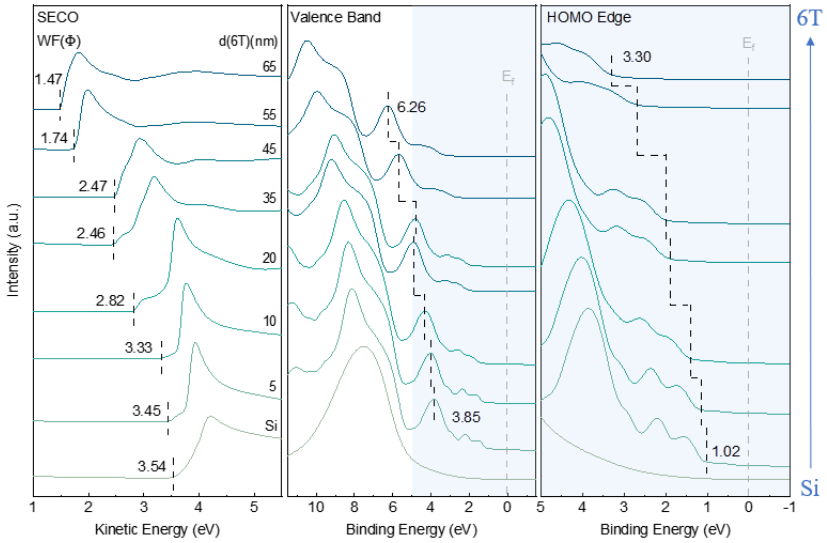

Figure S2. UPS spectra for increasing 6T deposition on a silicon substrate.

UPS spectra for increasing 6T deposition on a silicon substrate were studied to show the work function evaluation with different 6T thicknesses. As shown in Figure S2, with increasing 6T deposited, the work function value gradually decreases from 3.54 eV to 1.47 eV, which can become even lower with more 6T deposition. Similarly, the valence band peaks gradually shift to the higher binding energy side. In our experiments, the thickness of pre-deposited 6T layers on silicon substrates was characterized to be 19.1 nm through AFM characterization (Figure S3), which is reasonable for the films to have a work function of 2.85 eV.

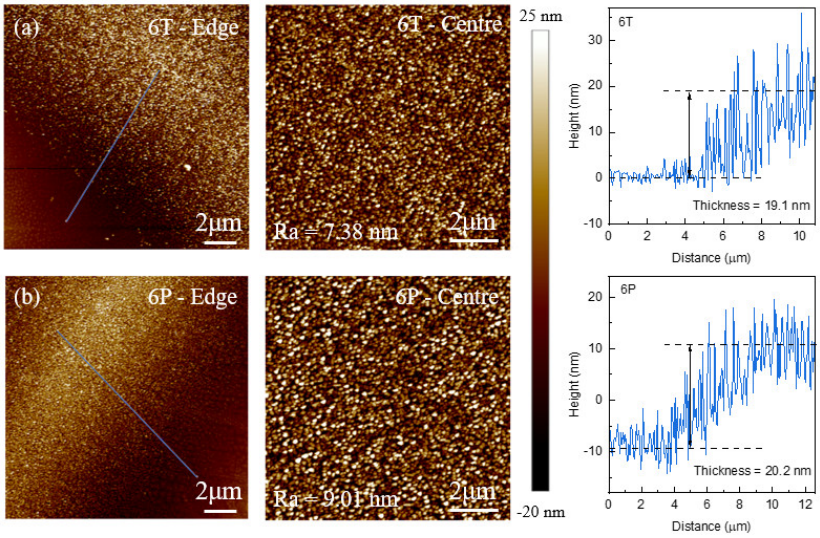

Figure S3. Thickness and surface morphology of (a) 6T and (b) 6P films characterized by AFM.

The thickness and surface morphology of 6T and 6P films on Si substrates was characterized by atomic force microscopy (AFM). The thicknesses of 6T and 6P films were about 19.1 nm and 20.2 nm, respectively. The average roughness (R_a) of 6T and 6P films was 7.38 nm and 9.01 nm, respectively.

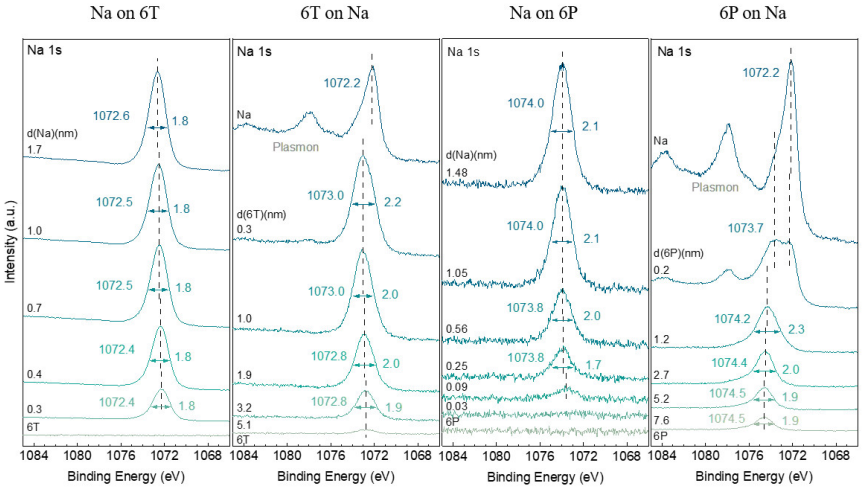

Figure S4. XPS spectra of Na 1s in different experiments: Na on 6T, 6T on Na, Na on 6P, and 6P on Na.

XPS spectra of Na 1s in different experiments are shown in Figure S4. For 6T-Na systems, when Na atoms are deposited on 6T molecules, the binding energy of Na 1s is slightly higher than that of pure Na metal, indicating that the Na atoms are partially oxidized. Additionally, the peaks at different Na deposition thicknesses have the same FWHM, indicating that the Na atoms interact with the same sites on 6T molecules during the deposition process. In the reverse deposition order experiment, the plasmon signals and the Na 1s peak at 1072.2 eV indicate the successful preparation of Na metal films. When 6T molecules are deposited on Na films, the FWHM of the peaks is larger than that of Na on 6T, indicating a more complex interaction process with an additional interaction site. For 6P-Na systems, when Na atoms are deposited on 6P molecules, since no chemical interaction occurs between Na and 6P, the deposited highly reactive Na metal can be oxidized by residual gases and contaminants over time, resulting in higher binding energy and a wider peak. In the reverse deposition order experiment, Na metal films are also successfully prepared. Due to the island 6P deposition

mode and a large number of Na atoms, the oxidization is stronger. The peaks at thin 6P deposition thicknesses have larger FWHMs because some unoxidized Na atoms remain.

Table S1. Detailed peak fitting parameters in C 1s and S 2p XPS core-level spectra for 6T with increasing Na deposition.

6T/Na		C 1s				S 2p					
		C_S	C_C	C_S-Na	C_S-Na_2	S_C		S_{Na1}		S_{Na2}	
						$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$
1.7 nm	BE (eV)	286.5	285.7	284.9	284.3	166.2	165.0	163.7	162.5	162.1	160.9
	FWHM	1.59	1.70	1.50	1.50	1.48	1.55	1.41	1.39	1.30	1.25
	Area (%)	22.2	50.0	20.0	7.8	15.1		35.3		49.6	
1.0 nm	BE (eV)	286.1	285.3	284.5	283.9	166.1	164.9	163.6	162.4	162.0	160.8
	FWHM	1.60	1.60	1.40	1.40	1.50	1.55	1.45	1.45	1.30	1.26
	Area (%)	26.9	50.0	18.0	5.1	28.2		36.5		35.3	
0.7 nm	BE (eV)	286.0	285.3	284.4	283.8	166.0	164.8	163.5	162.3	161.9	160.7
	FWHM	1.45	1.50	1.40	1.40	1.31	1.38	1.33	1.40	1.30	1.24
	Area (%)	31.6	50.0	15.3	3.1	43.4		29.9		26.7	
0.4 nm	BE (eV)	285.8	285.1	284.2	/	165.9	164.7	163.4	162.2	161.8	160.6
	FWHM	1.45	1.49	1.50	/	1.25	1.32	1.45	1.40	1.30	1.25
	Area (%)	38.0	50.0	12.0	/	65.2		21.7		13.1	
0.3 nm	BE (eV)	285.6	284.9	284.0	/	165.7	164.5	163.2	162.0	161.6	160.4
	FWHM	1.27	1.30	1.35	/	1.03	1.10	1.10	1.30	1.10	1.08
	Area (%)	45.8	50.0	4.2	/	86.7		9.7		3.6	
6T	BE (eV)	285.5	284.8	/	/	165.7	164.5	/	/	/	/
	FWHM	1.17	1.19	/	/	0.96	1.03	/	/	/	/
	Area (%)	50.0	50.0	/	/	100.0		/ /		/	

Table S2. Detailed peak fitting parameters in C 1s and S 2p XPS core-level spectra for Na with increasing 6T deposition.

Na/6T		C 1s				S 2p					
		C_S	C_C	C_S-Na	C_C-Na	S_C		S_{Na1}		S_{Na2}	
						$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$
Na	BE (eV)	/	/	/	/	/	/	/	/	/	/
	FWHM	/	/	/	/	/	/	/	/	/	/
	Area (%)	/	/	/	/	/		/		/	
0.3 nm	BE (eV)	286.5	285.7	285.0	283.4	166.4	165.2	164.6	163.4	162.7	161.5
	FWHM	1.50	1.70	1.55	1.67	1.60	1.40	1.60	1.41	1.53	1.65
	Area (%)	2.3	35.8	47.7	14.2	7.8		14.2		78.0	
1.0 nm	BE (eV)	286.5	285.8	285.1	283.3	166.2	165.0	164.4	163.2	162.5	161.4
	FWHM	1.60	1.60	1.54	1.60	1.49	1.41	1.35	1.49	1.57	1.57
	Area (%)	11.5	42.4	38.5	7.6	35.1		11.9		53.0	
1.9 nm	BE (eV)	286.3	285.6	284.9	283.3	166.2	165.0	164.4	163.2	162.4	161.2
	FWHM	1.50	1.44	1.50	1.50	1.46	1.40	1.30	1.50	1.30	1.48
	Area (%)	26.0	45.0	24.0	5.0	65.8		7.7		26.5	
3.2 nm	BE (eV)	286.2	285.4	284.7	/	166.1	164.9	164.3	163.1	162.3	161.1
	FWHM	1.31	1.36	1.50	/	1.40	1.42	1.30	1.50	1.30	1.50
	Area (%)	35.4	50.0	14.6	/	81.2		4.1		14.7	
5.1 nm	BE (eV)	286.0	285.3	/	/	166.1	164.9	/	/	/	/
	FWHM	1.36	1.40	/	/	1.33	1.34	/	/	/	/
	Area (%)	50.0	50.0	/	/	100.0		/ /		/	