# **Electronic Supplementary Information**

# Exploring the Difference of Bonding Strength between Silver(I) and Chalcogenide in Block Copolymer Systems

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# **1.** Experimental Procedures

## 1.1 Materials

Selenium powder, tellurium powder and sodium borohydride (NaBH<sub>4</sub>) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Poly (ethylene glycol) monomethyl ether (average Mw = 5000) was a product of Sigma-Aldrich Co., LLC (St. Louis). Silver(I) oxide, sodium sulfide (Na<sub>2</sub>S), 11-bromoundecanol and all deuterated solvents were purchased from J.K. Chemical (Beijing, China). 2,4-Toluene diisocyanate (TDI) was purchased from Tokyo Chemical Industry. Tetrahydrofuran (THF) was dried using sodium Type A (4 Å) molecular sieves. The solvents and chemicals were all used as received unless stated otherwise.

#### 1.2 Instruments and Methods

<sup>1</sup>H-NMR was performed using a BRUKER AVANCE III HD 400 (400 MHz) spectrometer (BRUKER, The Woodlands, TX). Electrospray ionization mass spectrometry (ESI-MS) spectrum was performed on a LTQ LC/MS apparatus. Gel permeation chromatography (GPC) measurements were recorded on the breeze system, Waters Corporation (styragel columns) (Milford, MA) with polystyrene as standard and dimethylformamide (DMF) as eluent. The X-ray Photoelectron Spectroscopy (XPS) measurements were taken on a ULVAC-PHI Quantro SXM. The samples were in powder forms. The time-of-flight secondary ion mass spectrometry (ToF-SIMS) were performed on an ION-TOF GmbH TOF.SIMS 5. The Contact Angle was measured by DSA30 from German Klux Co. Ltd. The

Raman spectroscopy was obtained from HORIBA Evolution with the excitation wavelength at 532 nm. The Atomic Force Microscope images were recorded from an Asylum Research Cypher S by tapping mode. ESI-mass was carried out on a LTQ LC/MS apparatus.

#### 1.3 Synthesis and characterization of HOC11X (X=S, Se, Te)

For the synthesis of HOC11S, 0.48 g (6.0 mmol) sodium sulfide (Na<sub>2</sub>S) and 10 mL deionized water were sequentially added into a 100 mL flask. The flask was sealed with a rubber plug and bubbled with N<sub>2</sub> for 10 min. Then, 3.0 g (12 mmol) 11-bromoundecanol (HOC11Br) dissolved in 15 mL anhydrous THF was injected into the flask under an atmosphere of N<sub>2</sub>. The reaction was performed at 50 °C for 12 h with stirring. After evaporation of THF, the crude product was extracted by  $CH_2Cl_2$  and deionized water to remove the water-soluble impurities. By evaporating to remove the  $CH_2Cl_2$  and dissolving in 5 mL THF, the concentrated liquid was added drop wisely to petroleum ether for recrystallization. The white powder of HOC11S was finally obtained with a yield of ~60%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 3.64 (4H, t, HO*CH*<sub>2</sub>), 2.50 (4H, t, S*CH*<sub>2</sub>), 1.68–1.20 (36H, m, HOCH<sub>2</sub>(*CH*<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>S) (Figure S10a).

Similar with the synthetic process of HOC11S, sodium hydro selenide (NaHSe) or disodium telluride (NaHTe) was reacted with 11-bromoundecanol to synthesize HOC11Se and HOC11Te compound. To acquire NaHSe, 0.48 g (6.0 mmol) Se powder, 0.90 g (12.0 mmol) of sodium borohydride (NaBH<sub>4</sub>), and 10 mL of deionized water were added into a 100 mL flask in sequence with the generation of H<sub>2</sub>. And Na<sub>2</sub>Te was obtained by placing 0.77 g (6.0 mmol) of Te powder, 0.90 g (12.0 mmol) sodium borohydride (NaBH<sub>4</sub>), and 10 mL of deionized water together into a 100 mL flask with the generation of H<sub>2</sub>. Later, the NaHSe and NaHTe were mixed with THF solution of HOC<sub>11</sub>Br at 50 °C for 12 h. The white powder of HOC11Se was obtained with a yield of ~60%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 3.64 (4H, t, HOC*H*<sub>2</sub>), 2.55 (4H, t, Se*CH*<sub>2</sub>), 1.71–1.20 (36H, m, HOCH<sub>2</sub>(*CH*<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>Se). The white powder of HOC11Te was obtained with a yield of ~60%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 3.64 (4H, t, Te*CH*<sub>2</sub>), 1.78–1.20 (36H, m, HOCH<sub>2</sub>(*CH*<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>Te) (Figure S10b and S10c).

The <sup>1</sup>H-NMR results of HOC11X (X=S, Se, Te) are consistent with relative reports of our previous work, in which <sup>13</sup>C NMR and mass spectrum results could also be found<sup>1,2</sup>.

#### 1.4 Synthesis and characterization of PEG-PUX-PEG (X=S, Se, Te)

The synthetic route of the three kinds of polymer were almost the same, therefore, the synthesis of PEG-PUS-PEG was introduced in detail as an example below. First, 0.47 g (1.25 mmol) di-(1-hydroxylundecyl) sulfide was dissolved in 5 mL anhydrous THF in a 25 mL flask. Then the flask was sealed with a rubber plug and bubbled with N<sub>2</sub> for 10 min. Next, 0.19 mL (1.35 mmol) TDI dissolved in 2 mL of anhydrous THF was injected into the flask under an atmosphere of N<sub>2</sub>. Later, the system was transferred into an oil bath at 50 °C to react with stirring. After 12 h, 1.2 g (0.24 mmol) PEG (M<sub>w</sub> = 5000) was dissolved in 2 mL anhydrous THF and injected into the flask, and the reaction proceeded for another 12 h. After recrystallization from petroleum ether, the solid residue was washed three times with deionized water and ethanol. Finally, 0.42 g of the white powder of PEG-PUS-PEG was finally obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.26 (3H, b, aromatic H), 4.15 (4H, b, NHCOO*CH*<sub>2</sub>), 3.64 (8H, b, O*CH*<sub>2</sub>*CH*<sub>2</sub> of PEG), 2.49 (4H, b, S*CH*<sub>2</sub>), 2.19 (4H, b, NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>), 1.70–1.10 (32H, b, NHCOO*C*H<sub>2</sub>*CH*<sub>2</sub>(*CH*<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>S); M<sub>n</sub>(NMR) = 10.35 × 10<sup>4</sup>, M<sub>w</sub>(GPC) = 8.15 × 10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub>(GPC) = 2 (Figure S11a and S11b).

Finally, 0.45 g white powder of PEG-PUSe-PEG was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$  (ppm): 7.26 (3H, b, aromatic H), 4.15 (4H, b, NHCOO*CH*<sub>2</sub>), 3.64 (8H, b, O*CH*<sub>2</sub>*CH*<sub>2</sub> of PEG), 2.54 (4H, b, Se*CH*<sub>2</sub>), 2.19 (4H, b, NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>), 1.70–1.10 (32H, b, NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>(*CH*<sub>2</sub>)<sub>8</sub>*CH*<sub>2</sub>Se); M<sub>n</sub>(NMR) = 12.65 × 10<sup>4</sup>, M<sub>w</sub>(GPC) = 8.17 × 10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub>(GPC) = 1.97 (Figure S11c and S11d).

Finally, 0.47 g white powder of PEG-PUTe-PEG was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$  (ppm): 7.26 (3H, b, aromatic H), 4.15 (4H, b, NHCOO*CH*<sub>2</sub>), 3.64 (8H, b, O*CH*<sub>2</sub>*CH*<sub>2</sub> of PEG), 2.62 (4H, b, Te*CH*<sub>2</sub>), 2.20 (4H, b, NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>), 1.78–1.22 (32H, b, NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>(*CH*<sub>2</sub>)<sub>8</sub>*CH*<sub>2</sub>Te); M<sub>n</sub>(NMR) = 12.02 × 10<sup>4</sup>, M<sub>w</sub>(GPC) = 2.70 × 10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub>(GPC) = 1.65 (Figure S11e and S11f).

The <sup>1</sup>H-NMR results of PEG-PUX-PEG (X = S, Se, Te) are consistent with those in our previous work<sup>1,2</sup>.

#### 1.5 Preparation of coordination compound

To obtain HOC11S+Ag<sup>+</sup> complex, 0.50 g (1.33 mmol) HOC11S, 0.28 g (1.46 mmol) AgBF<sub>4</sub>, and 2 mL methanol were added into 4 mL vial. After complete dissolution with ultrasound, the vial was placed into 37 °C thermostatic shaker for 12 h. Black precipitates were obtained by centrifugation and washed by methanol three times to remove the uncoordinated compound. Similar with the preparation process of HOC11S+Ag<sup>+</sup>, the black coordination compound of HOC11Se+Ag<sup>+</sup> and HOC11Te+Ag<sup>+</sup> were obtained.

#### 1.6 Preparation of self-assembled monolayer (SAM) formed by small molecules on silver substrates

Silver substrates were immersed in deionized water and anhydrous ethanol respectively with sonicating for 5 min. After drying the surface with  $N_2$ , the silver substrates were pretreated until hydrophilic with oxygen plasma for 5 s and were considered oxidized silver (I). Rapidly, the oxidized silver substrates were immersed in absolute ethanol for 30 s. Then the freshly prepared silver substrates were immersed in a 5 mM ethanolic solution of HOC11S, 5  $\mu$ M ethanolic solution of HOC11Se and HOC11Te respectively under  $N_2$  atmosphere for over 12 h at room temperature. Next, the substrates were rinsed with absolute ethanol and dried under a stream of high-purity nitrogen before further characterization.

#### 1.7 Single-molecule force spectroscopy (SMFS) experiments procedures

The force measurements were carried out on an Asylum Research Cypher S in contact mode. AFM cantilevers used here were commercially available V-shaped Si<sub>3</sub>N<sub>4</sub> cantilevers (Bruker) with a spring constant at 0.6 N/m according to the measurement of their thermal fluctuation. Prior to the force measurement, the tip was treated by piranha solution (7/3 v/v, 98% H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub>) for 2 min and followed by rinsing with water and dimethyl sulfoxide (DMSO). Meanwhile, tetrahydrofuran (THF) solution of PEG-PUX-PEG (X=S, Se, Te) (1  $\mu$ M) was injected to the surface of pretreated silver surfaces to form the coordination bond between Ag(I) and chalcogenide. After volatilization, DMSO was injected between the modified silver substrates and the cantilever holder, so the substrate and the cantilever were both immersed in the liquid. By controlling the movement of the piezo tube, the AFM tip was brought into contact with the substrate as shown in scheme 1. The tip tethered with PEG segment of PEG-PUX-PEG would settle for ca.1 s under a contact force of 1000 pN to ensure the formation of a PEG bridge between the tip and the substrate. Upon retracting the AFM tip from the substrate, the AFM cantilever was deflected and the PEG bridge was stretched. At the same time, a deflection-displacement curve was recorded and then converted into a force-extension curve (in brief, a force curve).

# 1.8 Rupture kinetics

The Dudko-Hummer-Szabo method was employed to transform rupture-force histograms into the force-dependent lifetimes (Figure S8). Consequently, the kinetic parameters of each Ag(I)-X bond can be calculated. Lifetime ( $\tau$ (F)) positively correlates with the height of the activation barrier, while  $\Delta x$  is the distance from the binding state to the transition state. The rupture forces were determined by both the height and width of the activation barrier as shown below.

$$\tau(F_{0} + (k - 1/2)\Delta F) = \frac{(h_{k}/2 + \sum_{i=k+1}^{N} h_{i})\Delta F}{h_{k}F(F_{0} + (k - 1/2)\Delta F)}$$
(1)  
$$\tau(F) = \tau_{0}exp\left(-\frac{F\Delta x}{k_{B}T}\right)$$
(2)

Where  $F_0$  is the starting force value of the histogram, N is the total number of the bins,  $\Delta F$  is the bin width,  $h_k$  is the ration of the bin number k, i and k is the number of each bin, F is the force loading rate,  $k_B$  is the Boltzmann constant, and T is the temperature in Kelvin.

According to formula 1 and 2, we can extract the rupture time  $\tau(F)$ , which was  $3.39 \times 10^{-5}$  s for Ag(I)-S,  $1.57 \times 10^{-4}$  s for Ag(I)-Se, and  $4.14 \times 10^{-3}$  s for Ag(I)-Te. The value of  $\Delta x$  was then calculated to be 0.138 nm for Ag(I)-S, 0.189 nm for Ag(I)-Se, and 0.276 nm for Ag(I)-Te. For the difference of  $\Delta x$  for Ag(I)-X (X = S, Se, Te), it was obvious that they were very close, which was reasonable because the length difference of Ag(I)-X bond was small according to the calculation. So the lengths to reach the transition states were very close. However,  $\tau(Ag(I)-Se)$  was nearly five times as much as  $\tau(Ag(I)-S)$ , which indicated that the strength of Ag(I)-Se bond was greater than that of Ag(I)-S since the rupture of Ag(I)-Se bond require higher force to reach its higher activation energy barrier compared with Ag(I)-S. In analogy,  $\tau(Ag(I)-Te)$  was more than twenty times as much as  $\tau(Ag(I)-Se)$  despite that  $\Delta x$  (Te) was just about 50 % larger than  $\Delta x$  (Se). Therefore, the rupture force of Ag(I)-Te should be more than that of Ag(I)-Se to reach higher energy barrier.

### **1.9** Computational details

Quantum chemistry calculations were performed using Density Functional Theory (DFT) to gain better insight into the Ag(I)-X bonding strength. The structural optimizations were carried out using the Vienna Ab-initio Simulation Package (VASP)<sup>3,4</sup> with the projector augmented wave (PAW) method<sup>5</sup> and a cutoff kinetic energy of 400 eV for plane-wave basis set. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional<sup>6</sup> was used. The atomic positions were supposed to be converged with convergence criteria of energy and force as  $1.0 \times 10^{-5}$  eV and 0.02 eV/Å, respectively. The reciprocal Brillouin zones were sampled by the  $\Gamma$  point as the unit cell is sufficiently huge. As confirmed by X-ray photoelectron spectroscopy in Figure S2a, the surface of silver was oxidized to the form of Ag(I) oxide. Besides, the main peak of silver surface is attributed to the (200) surface of Ag<sub>2</sub>O as presented in X-ray diffraction in Figure S2b. Thus, the 4 × 4 Ag<sub>2</sub>O (200) periodic slabs with a four-layer thick Ag-O were utilized in calculations, with the bottom two layers fixed to the bulk positions and the top two relaxed during geometry optimizations. As the chalcogenide-containing block copolymer PEG-PUX-PEG (Figure S6) used to explore the strength of silver(I)-chalcogenide (Ag(I)-X) interactions in the SMFS experiment is too big in size and time consuming in calculations, we simplify the model by reducing the number of CH<sub>2</sub> groups near the X atoms. So X(ROCONH<sub>2</sub>)<sub>2</sub> (X = S, Se, Te; R = CH<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub>) were used as the substitute of PEG-PUX-PEG to simplify the model structures and to save time for calculations. As the results are qualitatively similar, we only present the results with R = CH<sub>2</sub> here. Then various bonding configurations of X(CH<sub>2</sub>OCONH<sub>2</sub>)<sub>2</sub> on Ag<sub>2</sub>O (200) surfaces were considered to get the optimum structures. Therefore, quantum chemical calculations of X(CH<sub>2</sub>OCONH<sub>2</sub>)<sub>2</sub>/Ag<sub>2</sub>O (200) (X = S, Se, Te) were used to Ag-X interactions.

Periodic energy decomposition analysis (pEDA)<sup>7</sup> was performed by using the BAND code of the Amsterdam density functional package  $(ADF)^{8,9}$  to evaluate the bonding interactions between X(ROCONH<sub>2</sub>)<sub>2</sub> and the Ag<sub>2</sub>O support. The basis sets of uncontracted Slater-type orbitals (STOs) of triple zeta plus polarization (TZP) functions were applied<sup>10</sup>, with frozen core approximations to the inner shells [1s<sup>2</sup>] for C, [1s<sup>2</sup>-2p<sup>6</sup>] for S, [1s<sup>2</sup>-3p<sup>6</sup>] for Se, [1s<sup>2</sup>-4p<sup>6</sup>] for Te and [1s<sup>2</sup>-3d<sup>10</sup>] for Ag. The scalar relativistic (SR) effects were taken into account by the zero-order-regular approximation (ZORA)<sup>11</sup>.

# 2. Results and Discussion



# 2.1 Characterization of coordination compound (Ag/XC110H)<sup>+</sup> (X=S/Te)

*Figure S1.* (a) ESI-Mass spectrum of coordination compound, (b) NMR spectra (400 MHz, DMSO, 25 °C) and (c) XPS spectrum (S 2p and Te 3d) before and after coordination.



### 2.2 Characterization of pretreated surface of silver substrate

*Figure S2.* (a) From top to bottom: XPS spectrum of Ag 3d for the silver substrate before pretreating (black line), after pretreating (red line) and standard Ag<sub>2</sub>O powder (blue line). The binding energy of Ag 3d after pretreating reduced comparing with the value before pretreating and is almost the same as the value of standard Ag<sub>2</sub>O powder, which demonstrated that the surface of silver substrate was oxidized to the form of silver(I) oxide after pretreating, (b) From top to bottom: X-ray diffraction of silver after pretreating and standard spectrum of Ag<sub>2</sub>O powder <sup>[10]</sup>. The main peak of the pretreated surface of silver substrate is attributed to the (2 0 0) compared with the standard spectrum.

# 2.3 Characterization of self-assembled monolayer (SAM) on silver substrate



*Figure S3.* Characterization of self-assembled monolayers (SAMs) on the silver surface. XPS (**a**) S 2p, (**b**) Se 3d, and (**c**) Te 3d peaks of HOC11X (X=S, Se, Te) modified silver surfaces respectively.

Counts	Ag(I)	Ag(I)-SAM	
S <sup>-</sup>	5.8×10 <sup>5</sup>	3.6×10 <sup>6</sup>	
Se	<b>6.9×10</b> <sup>3</sup>	5.3×10 <sup>5</sup>	
Te	<b>1.6</b> ×10 <sup>3</sup>	4.5×10 <sup>4</sup>	

2.4 Quantifications of HOC11X modified silver substrates (X=S/Se/Te) by ToF-SIMS

*Table S1.* Total counts of S<sup>-</sup>, Se<sup>-</sup> and Te<sup>-</sup> of HOC11X (X=S/Se/Te) modified silver substrates respectively.

2.5 Morphology characterization of SAMs on the silver surface



*Figure S4.* AFM phase image of unmodified silver (a), HOC11S (d), HOC11Se (g), and HOC11Te (j) modified silver surfaces. AFM image in two dimensions and three dimensions of (b) and (c) unmodified silver, (e) and (f) HOC11S, (h) and (i) HOC11Se, and (k) and (l) HOC11Te modified silver surfaces. And the roughness of unmodified silver, HOC11S, HOC11Se, and HOC11Te modified silver surface was  $1.6\pm0.2$  nm,  $1.7\pm0.1$  nm,  $1.8\pm0.1$  nm, and  $1.9\pm0.1$  nm, respectively.

# 2.6 Raman evidence of the coordination bonds



*Figure S5.* Raman spectra of (a) HOC11X (X = S, Se, Te) at the range of 550-800 cm<sup>-1</sup>. Full Raman spectra of (b) HOC11X and (c) SAMs composed of HOC11X (X = S, Se, Te) formed on silver surfaces.

# 2.7 Chemical structure of chalcogenide-containing block copolymers



*Figure S6.* PEG-PUX-PEG synthesized for measuring bond strength of Ag(I)-X bonds (X = S, Se, Te).

# 2.8 Results of single molecule force spectroscopy (SMFS) experiment



*Figure S7.* Typical F-E curves of detaching individual PEG-PUX-PEG molecules from silver substrate. From left to right, X = S, Se, Te, respectively.



2.9 Rupture kinetics of Ag-X bonds

*Figure S8.* Lifetime-force curves for detaching individual PEG-PUX-PEG molecules from the silver substrates. From bottom to top, X=S, Se, Te, respectively.

2.10 Table S2. Optimized bond lengths of Ag-X and X-C, bond angles of C-Ag-C and Hirshfeld net charges of  $[X(CH_2OCONH_2)_2]$  in  $X(CH_2OCONH_2)_2/Ag_2O(200)$  (X = S, Se, Te).

Х	Ag–X (Å)	X-C (Å)	∠C–Ag–C (°)	Charge
S	2.58(2.31) <sup>a</sup>	1.84	100.8	0.20
Se	2.64(2.44) <sup>a</sup>	2.01	97.0	0.22
Те	2.72(2.64) <sup>a</sup>	2.22	93.0	0.27

<sup>a</sup> The values in parentheses correspond to the Ag-X covalent single-bond lengths raised by Pyykkö.



2.11 Projected density of states (PDOS) for  $XR_2/Ag_2O(200)$  (X = S, Se, Te; R = CH<sub>2</sub>OCONH<sub>2</sub>).

*Figure S9.* PDOS diagram for the Ag atom that bind with X (Ag<sub>a</sub>), the X atom and the XR<sub>2</sub> molecule. The dominate orbital interactions between Ag<sub>a</sub> and SR<sub>2</sub> locate between -3.5 and -2.5 eV, while increased interactions are observed between -4.0 and -3.5 eV for Se(CH<sub>2</sub>OCONH<sub>2</sub>)<sub>2</sub>/Ag<sub>2</sub>O (200), indicating that the Ag-Se bond is stronger than Ag-S. Besides, obvious orbital interactions are found for Te(CH<sub>2</sub>OCONH<sub>2</sub>)<sub>2</sub>/Ag<sub>2</sub>O (200) between -5.5 and -4.0 eV, demonstrating the enhanced bond strength of Ag-Te. Therefore, as X becomes heavier, the Ag-X bond strength will increase with enhanced orbital interactions at the lower energy range below the Fermi level.





*Figure S10.* (a) HOC11S. (b) HOC11Se. (c) HOC11Te. The <sup>1</sup>H-NMR results of HOC11X (X = S, Se, Te) are consistent with our previous work <sup>[11,12]</sup>.

2.13 <sup>1</sup>H NMR and GPC characterization of the PEG-PUX-PEG



*Figure S11.* <sup>1</sup>H-NMR (400M CDCl<sub>3</sub>) of the (a) sulfide-, (c) selenide-, and (e) telluride-containing polymers PEG-PUX-PEG. GPC plot of (b) PEG-PUS-PEG, (d) PEG-PUSe-PEG, and (f) PEG-PUTe-PEG polymer.

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