

Supplementary Material

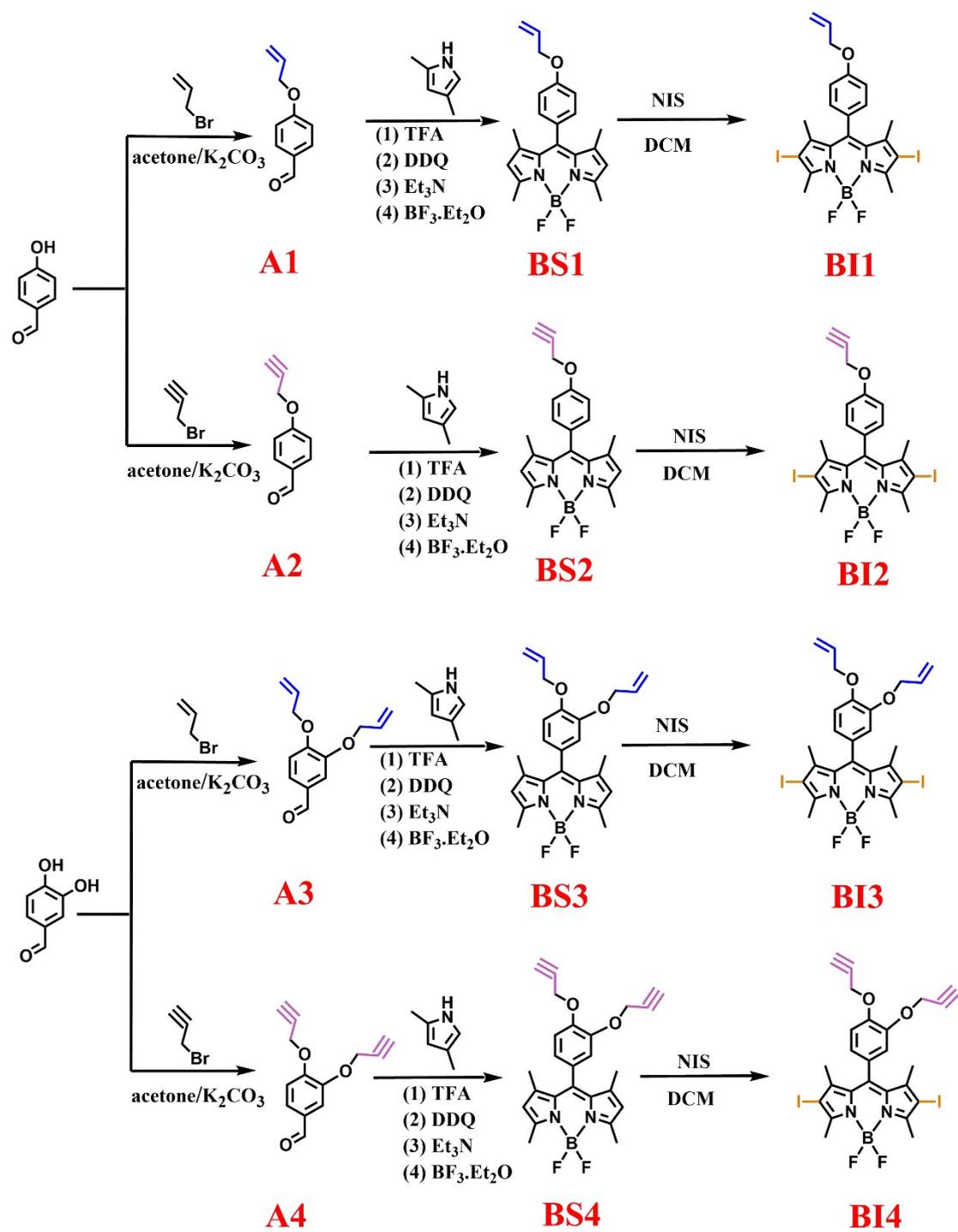
Reaction-based fluorescent silk probes with high sensitivity and selectivity to Hg²⁺ and Ag⁺ ions

Li Xiao^a, Kaiqi Liu^a, Lian Duan^{b*}, Xinjian Cheng^{a*}

^aSchool of Chemistry and Environmental Engineering, Wuhan Institute of
Technology, Wuhan, China, 430073

^bSchool of Textiles and Garments, Southwest University, Chongqing, 400715, PR
China

*Corresponding author: Dr. Duan, duan19850420@163.com; Dr. Cheng,
chxj606@163.com.



Scheme S1. Synthetic route of small molecule compounds

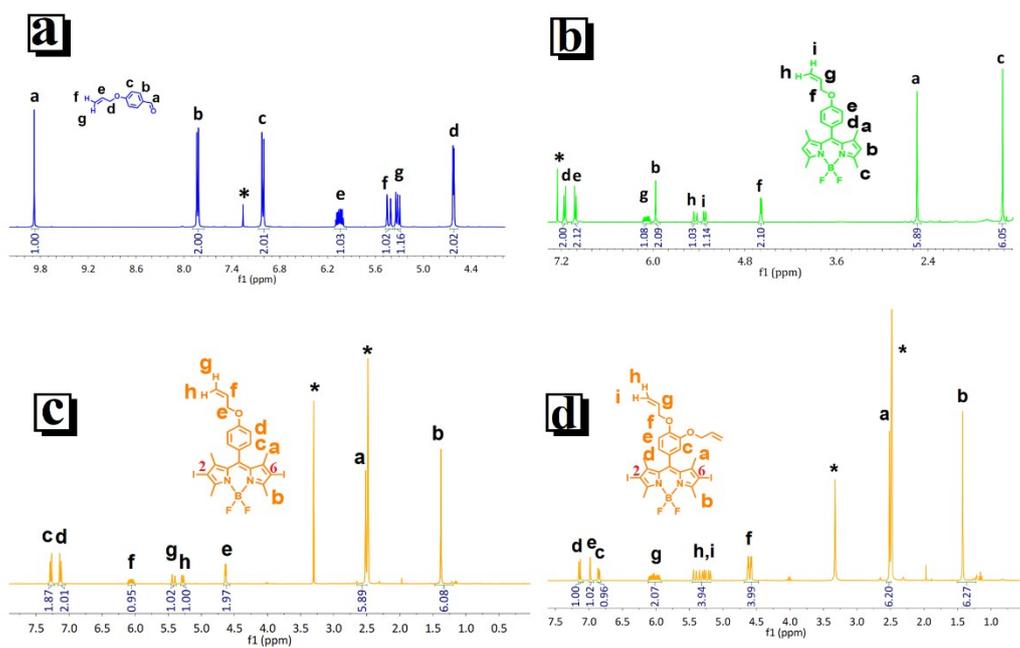


Figure S1. ^1H NMR spectra of small molecule compounds (a) A1, (b) BS1, (c) BI1, and (d) BI3

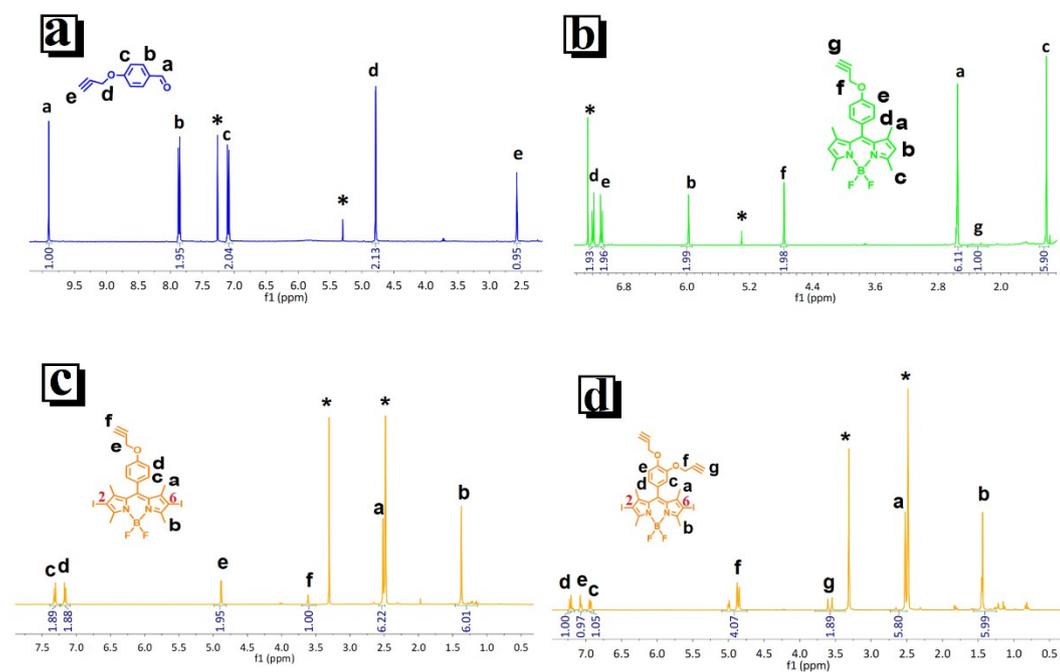


Figure S2. ^1H NMR spectra of small molecule compounds (a) A2, (b) BS2, (c) BI2, and (d) BI4

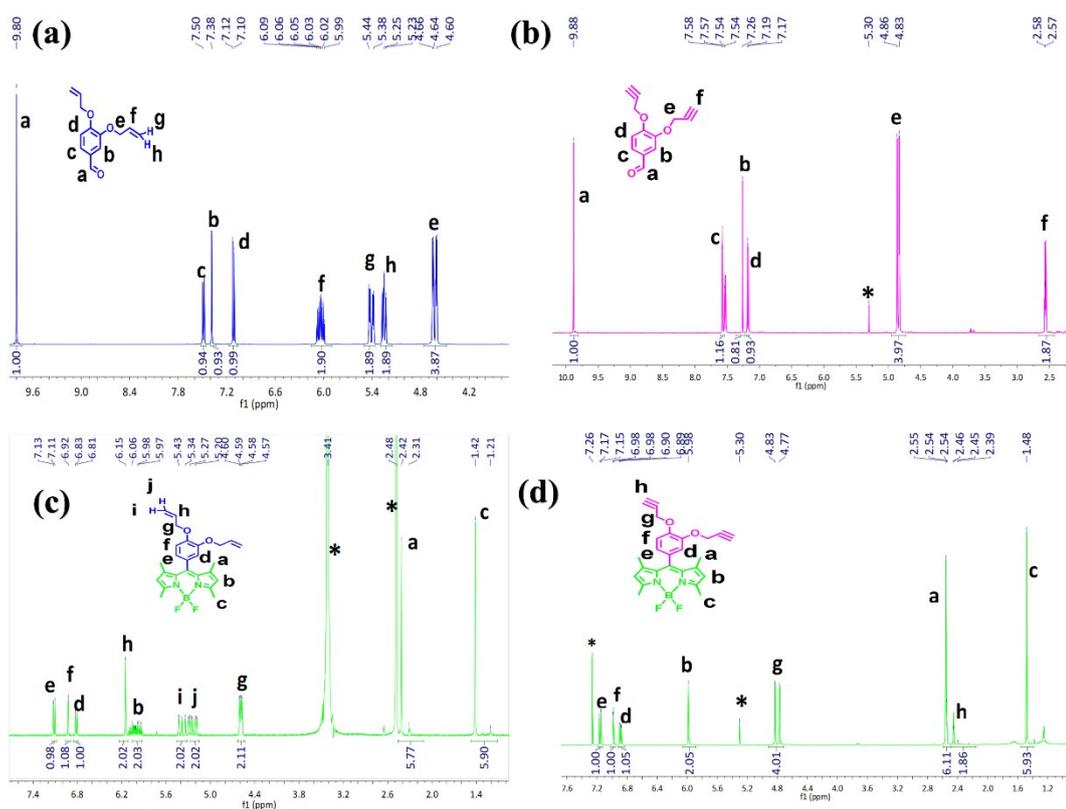


Figure S3. ^1H NMR spectra of small molecule compounds (a) A3, (b) A4, (c) BS3, and (d) BS4

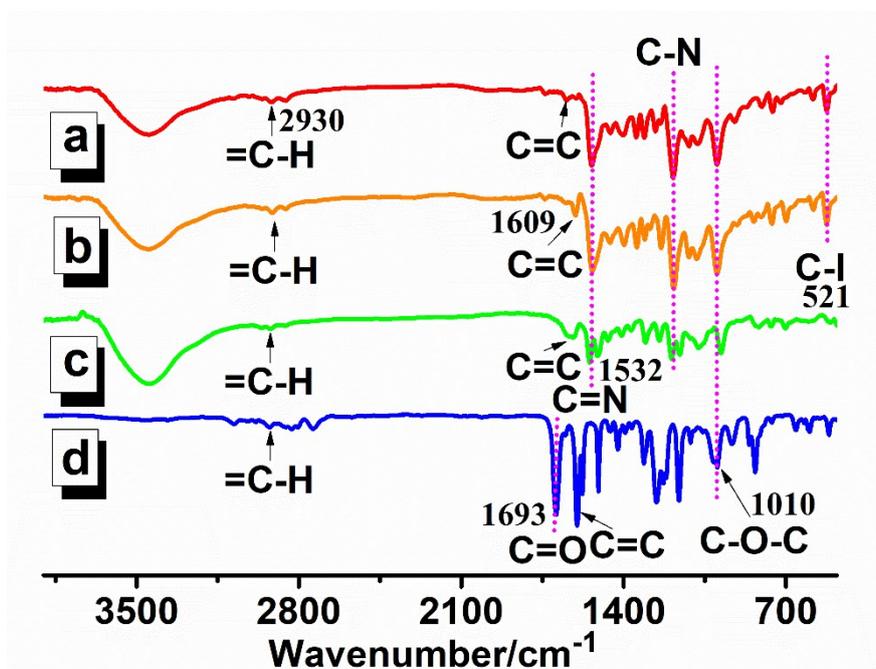


Figure S4. FTIR spectrum of (a) BI3, (b) BI1, (c) BS1, and (d) A1

Sample Name	Sample8	Position	P1-A8	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	WYZ-1.d	ACQ Method	Default-TEST.m	Comment		Acquired Time	11/26/2019 10:26:34 AM

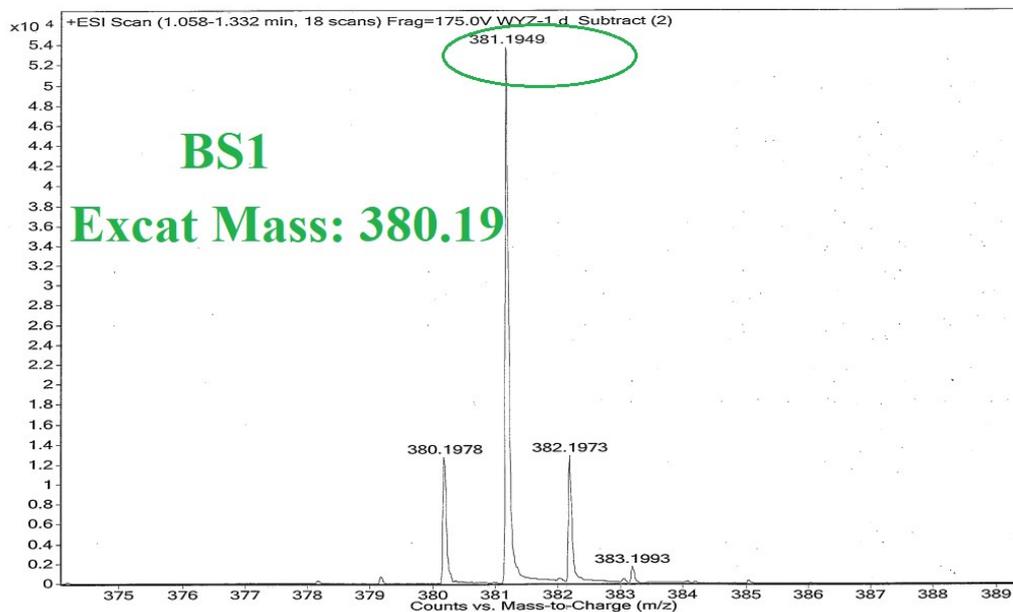


Figure S5. ESI-HRMS spectrum of BS1

Sample Name	Sample4	Position	P1-A4	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	XL-4.d	ACQ Method	Default-TEST.m	Comment		Acquired Time	9/17/2020 3:50:13 PM

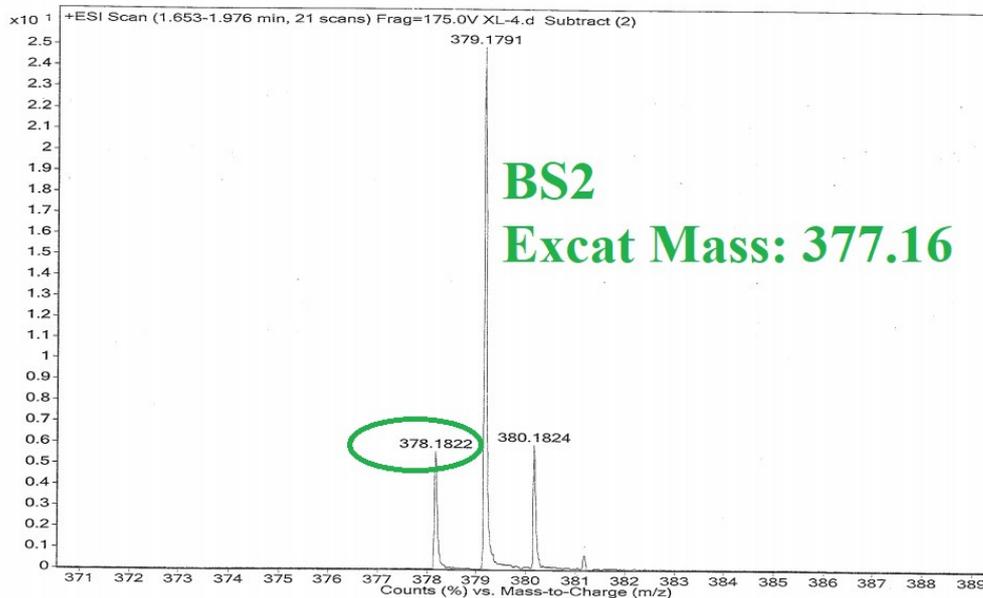


Figure S6. ESI-HRMS spectrum of BS2

Sample Name	Sample9	Position	P1-A9	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	WYZ-2.d	ACQ Method	Default-TEST.m	Comment		Acquired Time	11/26/2019 10:33:28 AM

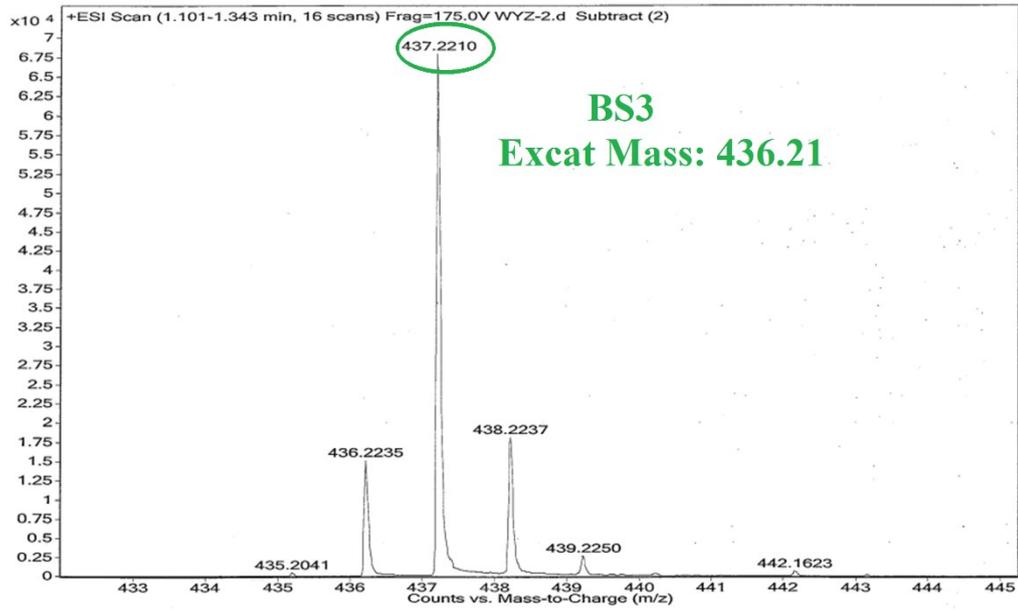


Figure S7. ESI-HRMS spectrum of BS3

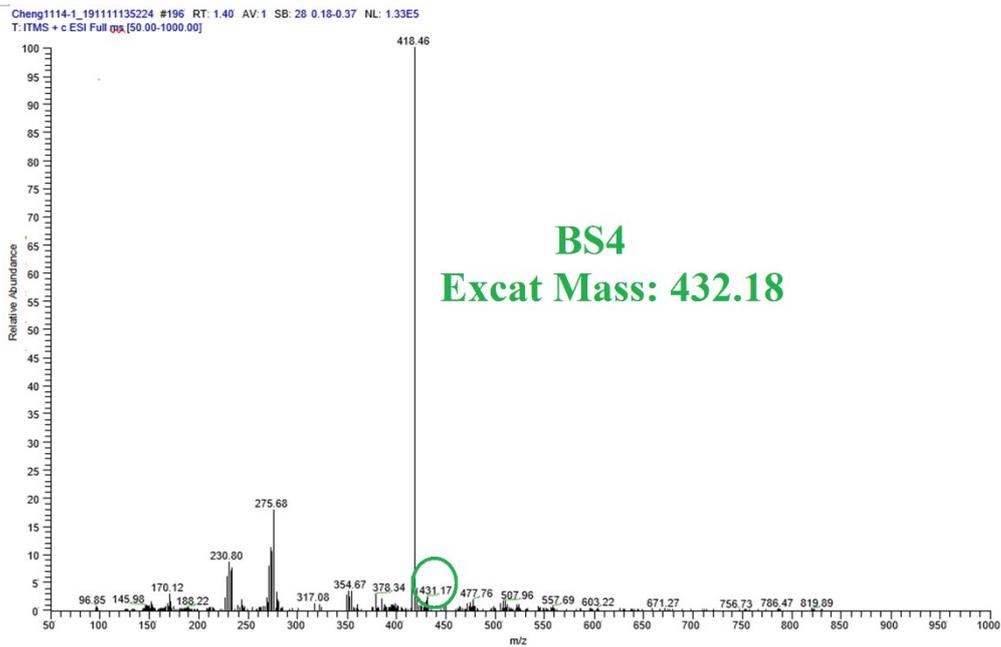


Figure S8. ESI-HRMS spectrum of BS4

Ch1021-1_201022200650 #91 RT: 0.94 AV: 1 SB: 36 0.11-0.48 NL: 2.30E3
T: ITMS + c ESI Full ms [50.00-2000.00]

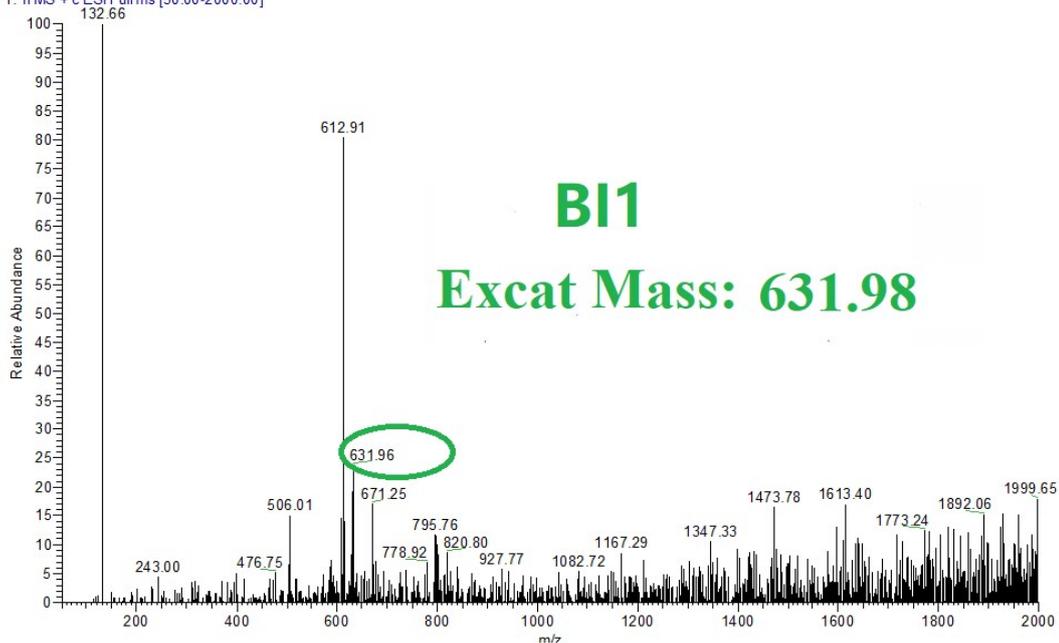


Figure S9. ESI-HRMS spectrum of B11

Ch1021-2_201022200650 #272 RT: 2.82 AV: 1 NL: 2.46E3
T: ITMS + c ESI Full ms [50.00-2000.00]

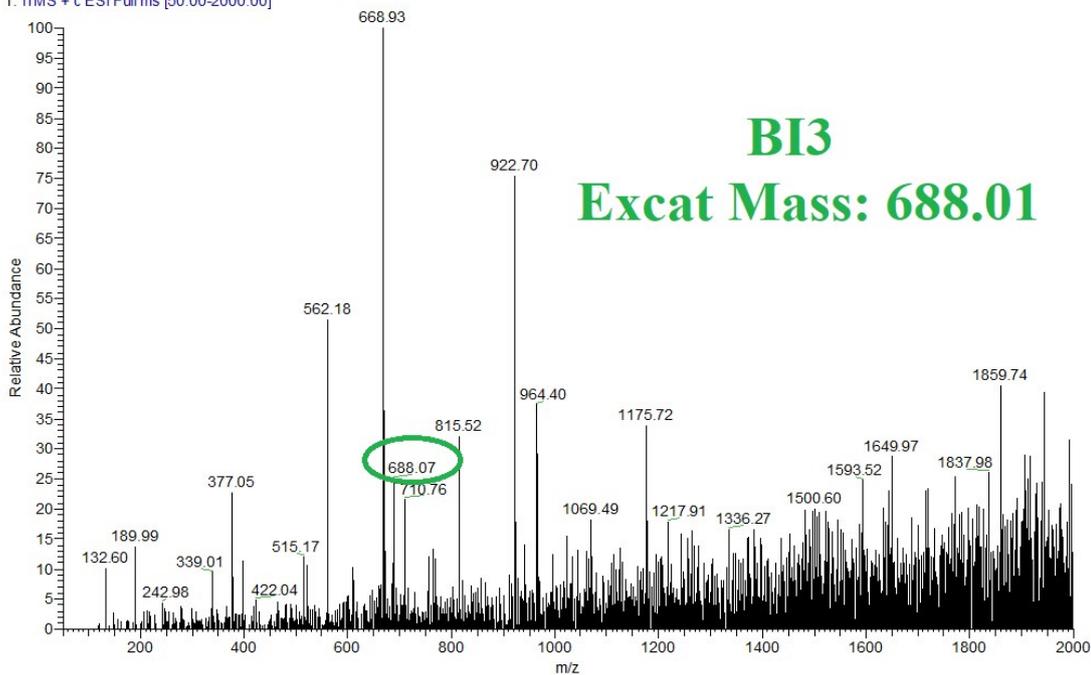
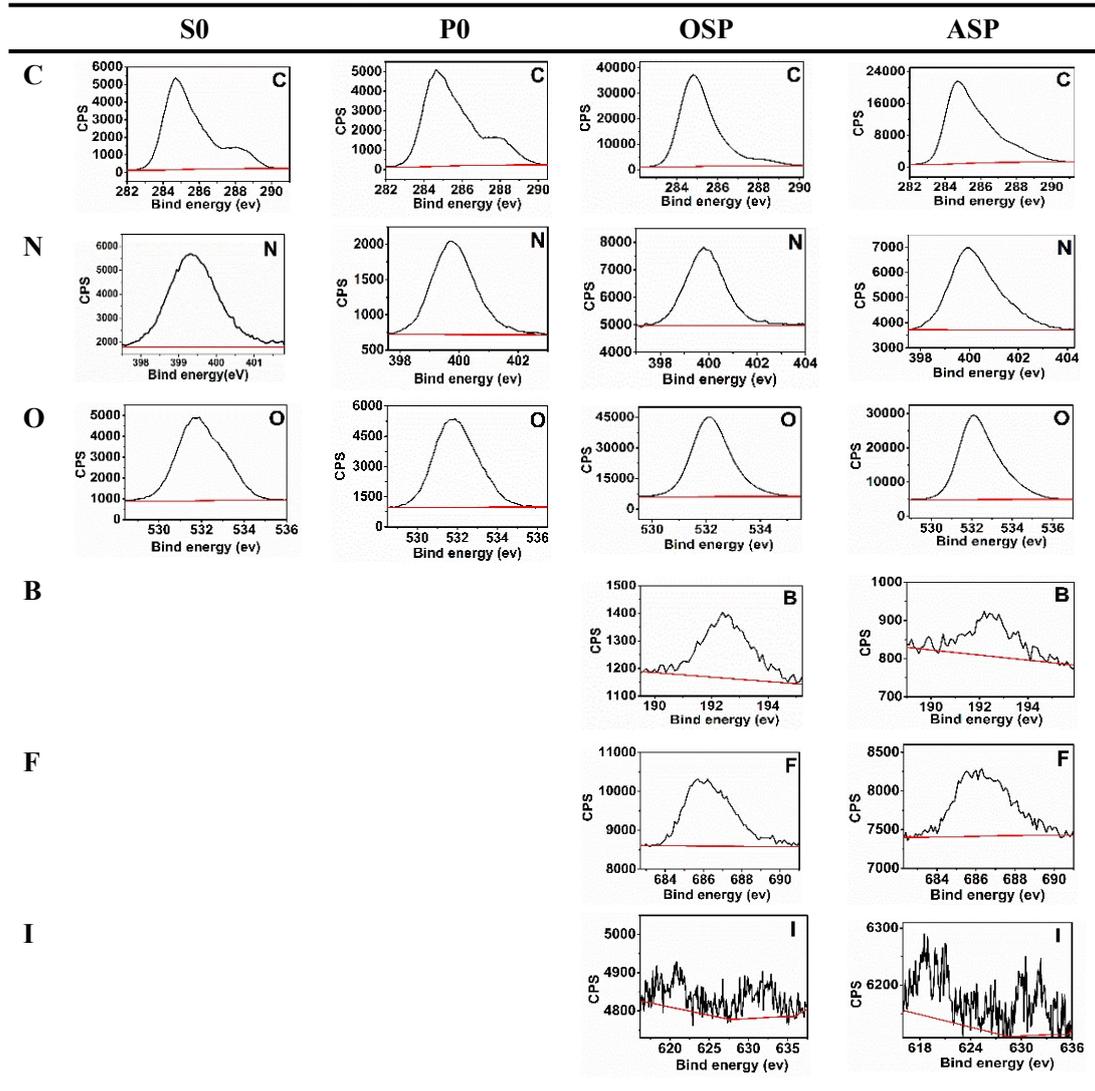


Figure S10. ESI-HRMS spectrum of B13

Table S1. Distribution of XPS spectra for untreated silk (S0, P0) and fluorescent silk (OSP, ASP)



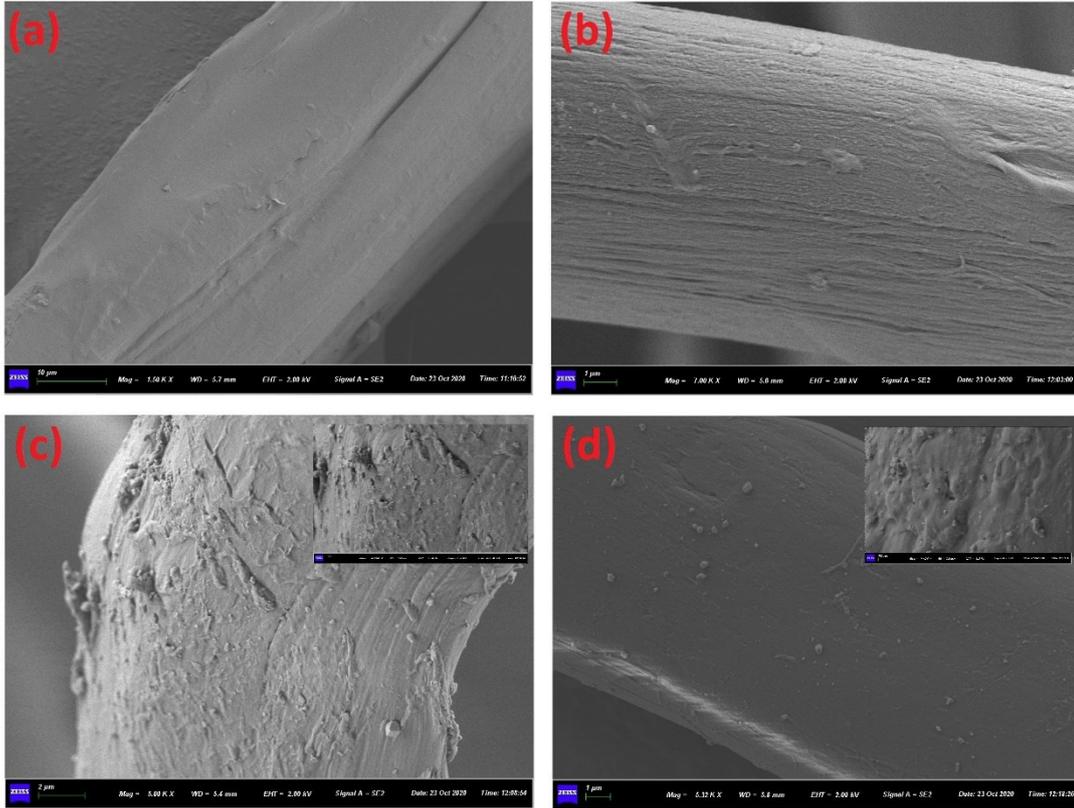


Figure S11. SEM micrographs and partial enlarged photos of silk (a) un-degummed silk **S0**, (b) degummed silk **P0**, (c) fluorescent silk **OSP**, and (d) fluorescent silk **ASP**

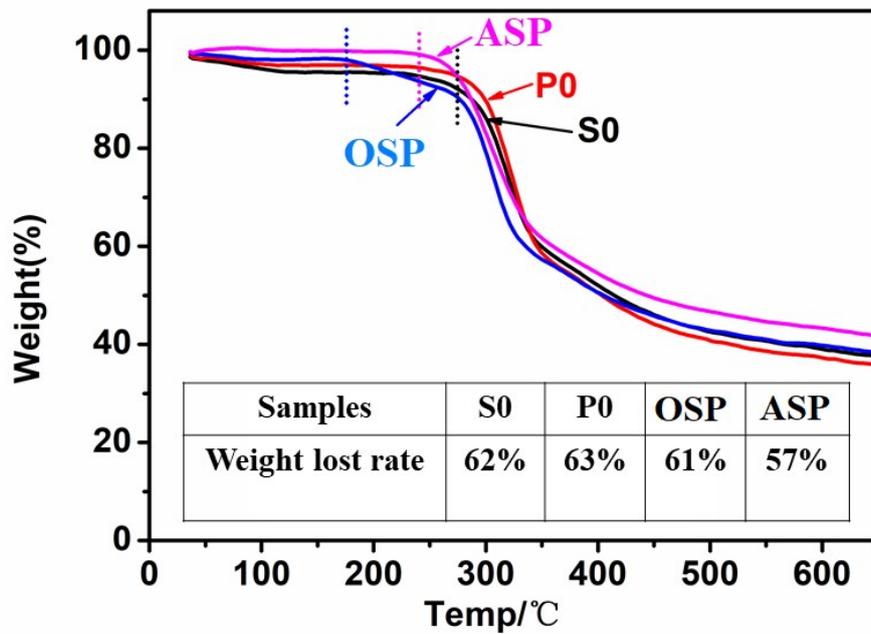


Figure S12. TGA curves of un-degummed silk (**S0**), degummed silk (**P0**), fluorescent silk (**OSP** and **ASP**)

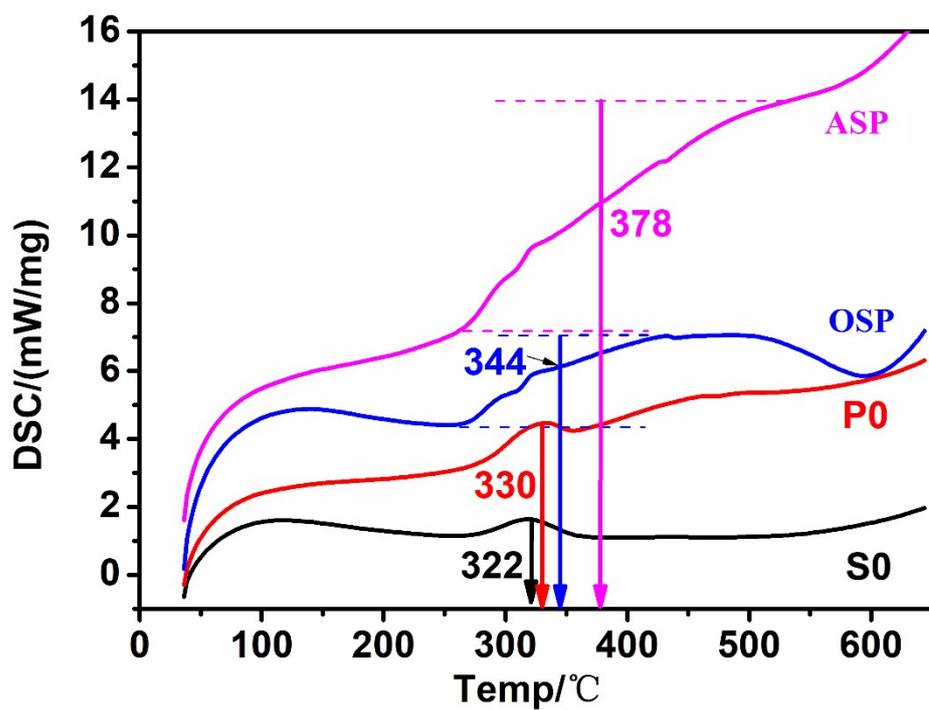


Figure S13. DSC curves of un-degummed silk (S0), degummed silk (P0), fluorescent silk (OSP and ASP)

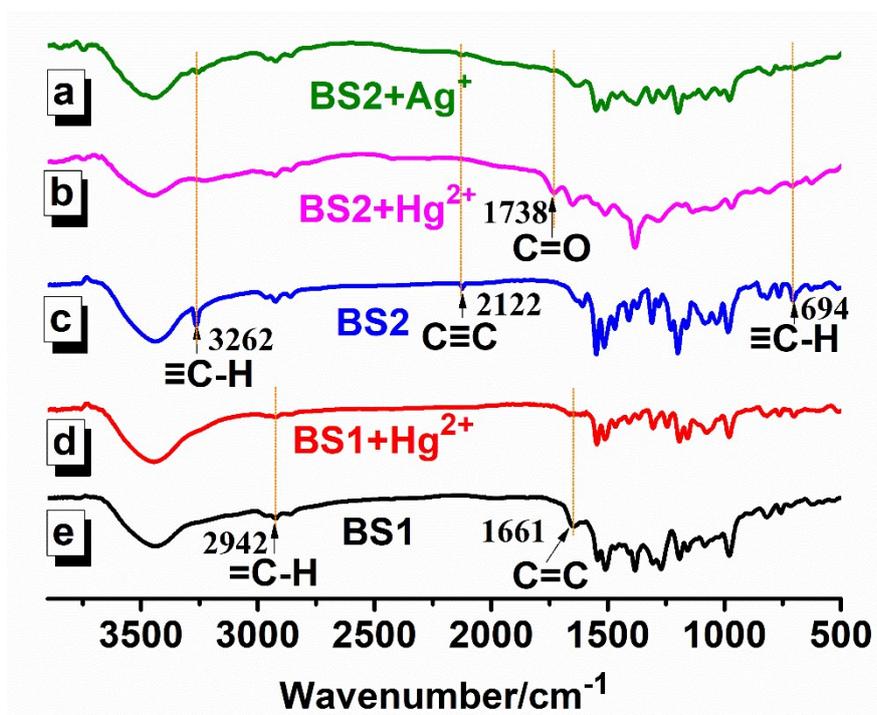


Figure S14. FTIR spectra of (a) BS2+Ag⁺, (b) BS2+Hg²⁺, (c) BS2, (d) BS1+Hg²⁺, and (e) BS1

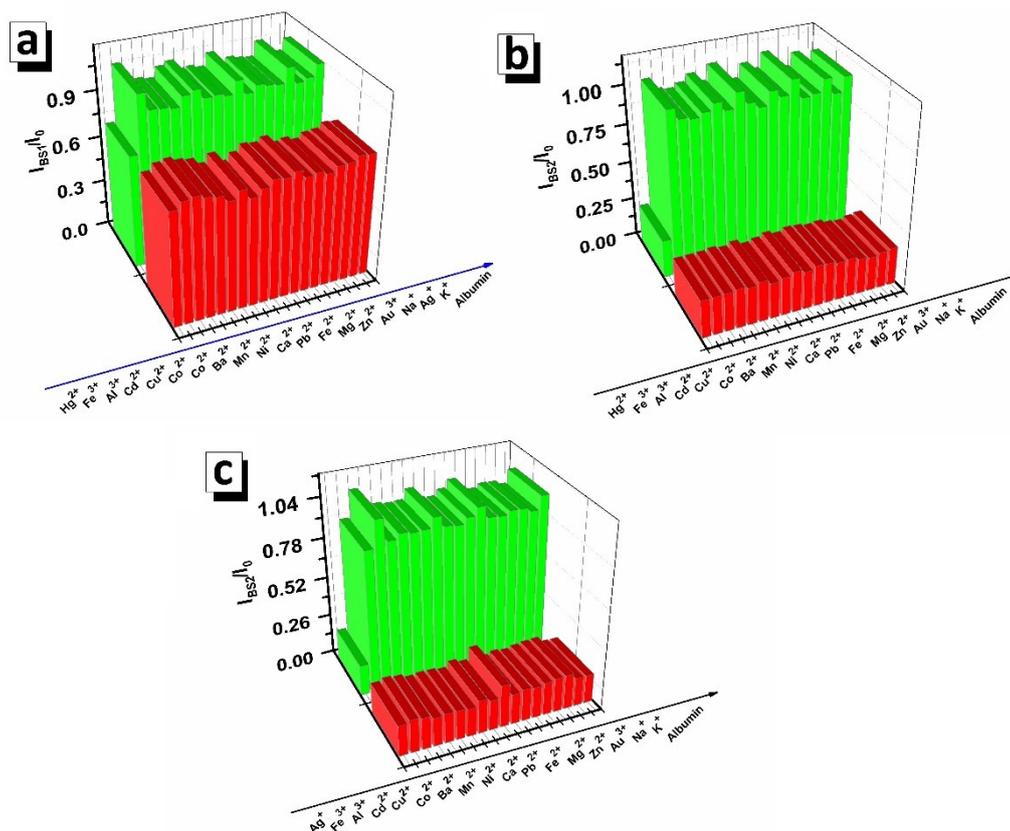


Figure. S15 (a) Fluorescence response of **BS1** to other metal ions and bovine serum albumin in the presence of Hg^{2+} (b) Fluorescence response of **BS2** to other metal ions and bovine serum albumin in the presence of Hg^{2+} (c) Fluorescence response of **BS2** to other metal ions and bovine serum albumin in the presence of Ag^+

Table S2. Comparison of Hg^{2+} adsorption by untreated silk (**P0**) and fluorescent silk (**OSP/ASP**)

	P0	OSP	ASP
Initial Hg^{2+} mg/L (C_0)	351	351	351
Remain Hg^{2+} mg/L (C)	123	28.5	96.9
Average quality of samples mg (m)	43.45	51.5	35.4
Adsorption efficiency $\% \cdot \text{mg}^{-1}$ (η)	1.49	1.78	2.05
Hg^{2+} content tested by XPS (%)	-	0.89	1.13

$$\eta = \frac{C_0 - C}{C_0 * m}$$

Table S3. Comparison and evaluation of the basic properties of the reported sensors and sensors synthesized in this work

Sensor	LOD	Selectivity	Kinetics	Applications	Reference
Cy-PT	0.18 μM	Excellent (Hg^{2+})	Rapid response	Living cells and zebrafish	46
OTA-DCM	0.14 μM	High (Hg^{2+})	Rapid response	Living cells and zebrafish larvae	47
TBBA	13.10 nM	Sensitive (Hg^{2+})	-	Living cells and zebrafish	48
NPPI	3.86 μM	High (Ag^+)	Rapid response	Living cells and zebrafish larvae	49
BS4	0.25/0.83 μM	Sensitive ($\text{Ag}^+/\text{Hg}^{2+}$)	-	Aqueous adsorbent	this work

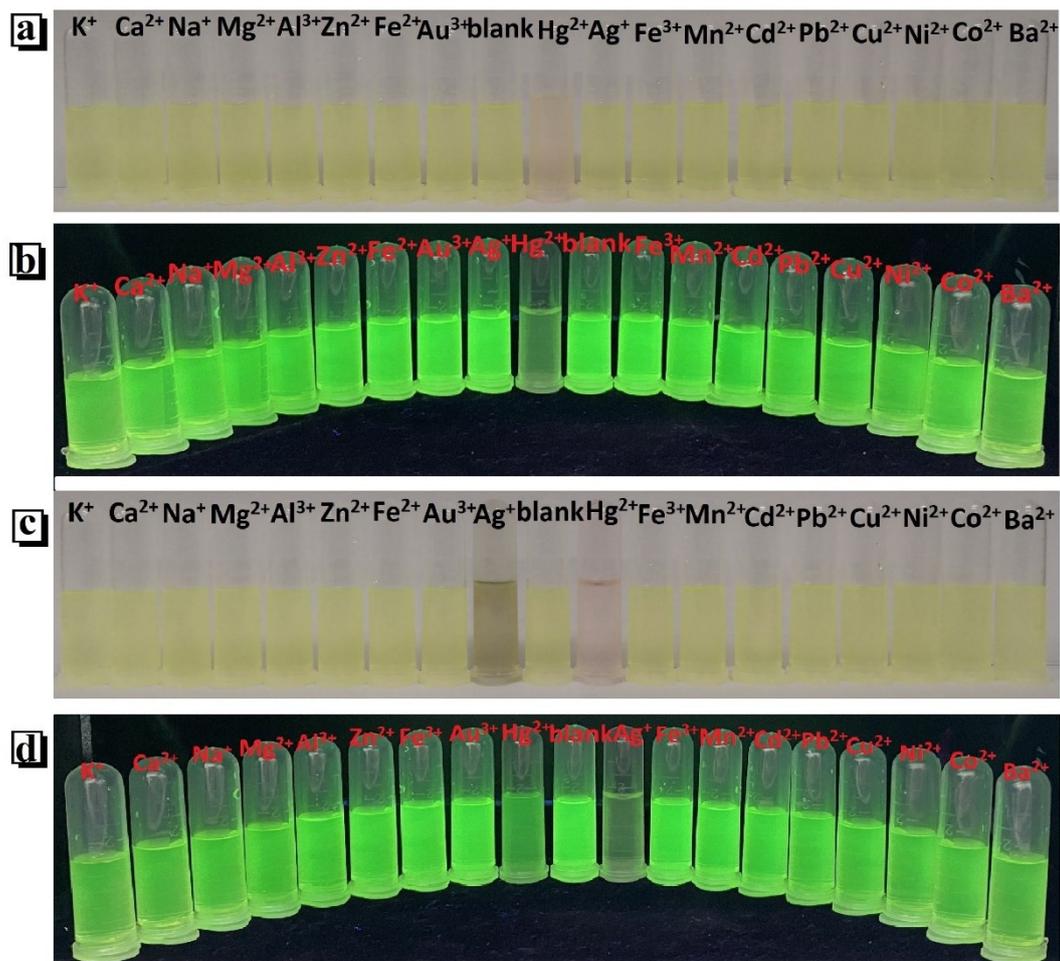
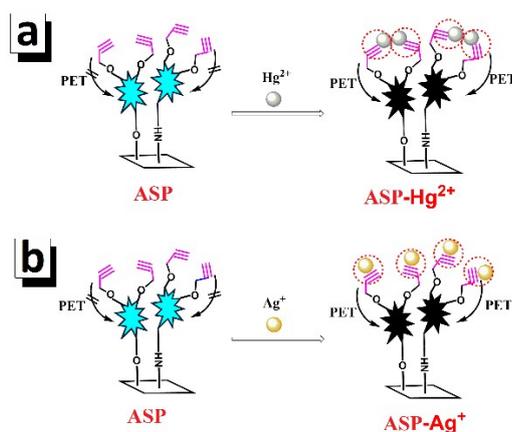


Figure. S16 (a) Photographs of **BS1** (10 μM) with heavy metal ion in DMF under natural light and (b) UV light. (c) Photographs of **BS2** (10 μM) in DMF under natural light and (d) UV light



Scheme S2. Structural representation of the binding sites of (a) **ASP-Hg²⁺**, (b) **ASP-Ag⁺**