Supporting Information for

Highly Sensitive Colorimetric Photonic Sensors for Specific Heavy Metal Ions Detection

By *Wei Hong*, Weihua Li, *Xiaobin Hu**, *Binyuan Zhao*, *Fan Zhang** and *Di Zhang**

Formula for Preparation of Ions-Sensitive Photonic Film:

Cu-sensitive photonic film: Cupric hydroxide (48.5 mg, 0.5 mmol) was added to a solution of AMPS (208 mg, 1 mmol) in 150 μl water. After the dissolution of cupric hydroxide, 700 μl ethanol, 450 μl PEG170-DMA (ca. 1.5 mmol), 215 μl 4-vinylpyridine (2 mmol) and 15 μl HMPP were added to the former Cu-AMPS solution. The final solution was stirred at ambient temperature for 10 minutes, and should be used immediately. Or else cupric hydroxide would begin to form again in the following two hours because pyridine is not such a strong ligand that can dissolve cupric hydroxide.

Imidazole-photonic film: 1-vinylimidazole was used as a substitute for 4-vinylpyridine. Procedures for the preparation were operated similar to the Cu-sensitive photonic film, except that basic nickel carbonate was used instead of cupric hydroxide because we found that the imizazole-Cu2+ complex compound was a polymerization terminator.

PEG-photonic film: 246.3 mg PSM (1 mmol), 84 mg APMS (0.4 mmol), 56 μl triethylamine (0.4 mmol), 116 μl styrene (1 mmol), 500 μl PEG400-DMA (ca. 1 mmol) and 5 mg AIBN were mixed in a mixing solvent of 800 μl ethanol and 100 μl water.

Pb-sensitive photonic film: 246.3 mg PSM (1 mmol), 64 μl methyl methacrylate (0.6 mmol), 169.2 mg 4-Vinylbenzo-18-crown-6 (0.5 mmol), 300 μl PEG170-DMA (ca. 1 mmol) and 5 μl HMPP were mixed in a mixing solvent of 350 μl ethanol and 350 μl water.

Ag-sensitive photonic film: 246.3 mg PSM (1 mmol), 106 μl methyl methacrylate (1 mmol), 13 μl GMA (0.1 mmol), 300 μl PEG170-DMA (ca. 1 mmol) and 5 μl HMPP were mixed in a mixing solvent of 350 μl ethanol and 350 μl water.

Preparation of Thiourea-Formaldehyde Prepolymer: Thiourea-formaldehyde (TF) prepolymer was synthesized according to amine-formaldehyde reactions.19 The molar ratio of thiourea to formaldehyde was used as 1:1 in this study. In a flask, 9.38 g of thiourea (123.2 mmol) was mixed with 10 g of formaldehyde solution (c.a. 123 mmol). NaOH was added into the mixture so that the pH was increased to 8-8.5. The mixture was heated at around 353 K until all thiourea was dissolved. The syntheses were continued by acid-catalyzed condensation reaction by adding HCl solution until pH at 4.8-5. The reaction went on for another one hour, and then the mixture was cooled to room temperature in air. The obtained TF prepolymer was a clear and transparent colorless solution.

Table S1. Comparison of Ammonia, Imidazole and Pyridine by Logarithms of Stability Constants

Ligand		H^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ag^+
NH_3 [a]	K_1	9.33	2.11	2.80	4.15	2.37	2.65	3.2
	K_2		1.63	2.24	3.50	2.44	2.10	3.8
	K_3		1.05	1.73	2.89	2.50	1.44	
	K_4		0.76	1.19	2.13	2.15	0.93	
Imidazole [b]	K_1	7.11	2.45	3.0	4.2	2.52	2.8	3.1
	K_2		1.9	2.5	3.42	2.32	2.1	3.8
	K_3		1.4	2.0	2.88	2.32	1.55	
	K_4			1.5	2.1	2.0	1.1	
	β_4		**5.75(β_3)**	**9.0**	**12.6**	**9.16**	**7.55**	
Pyridine [c]	K_1	5.21	1.15	1.78	2.41	0.88	1.30	2.0
	K_2		0.55	1.22	1.88	0.47	0.84	2.2
	K_3		-0.3	0.3	1.14	0.15	0.36	
	K_4			-0.3	0.60	-0.2	-0.2	
	β_4		**1.4(β_3)**	**3.00**	**6.03**	**1.30**	**2.3**	
Pyridine [d]	β_1		1.14		2.59	1.41	1.40	
	β_2		1.54		4.33	1.11	1.95	
	β_3				5.93	1.61	2.27	
	β_4				**6.54**	**1.93**	**2.50**	
	β_5				**7.00**			
	β_6				**10.2**			

k stands for stepwise stability and β stands for overall stability.

[a] values in 2 M NH_4NO_3 and 30° .[1]

[b] values near 0.2 ionic strength and 25° .[1]

[c] values at 25° and 0.5 ionic strength.[1]

[d] values at 25° and ionic strengths approaching zero.[2]

Table S2. Logarithms of Stability Constants of Thourea Complex

Ligand		Ag^{+}	Cd^{2+}	Cu^{+}	Hg^{2+}	Pb^{2+}	Ru^{3+}
Thiourea	β_1	7.4	0.6			1.4	1.21
	β_2	13.1	1.6		22.1	3.1	
	β_3		2.6	13	24.7	4.7	0.72
	β_4		4.6	15.4	26.8	8.3	

All value at 25° and ionic strengths approaching zero. [2]

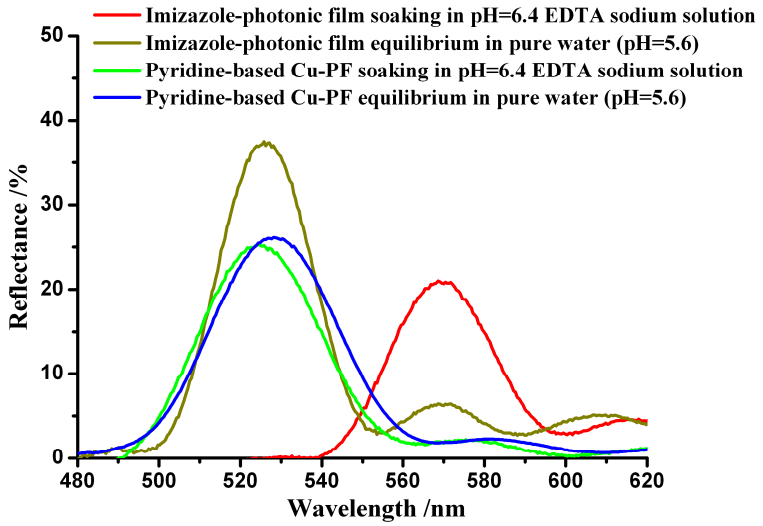
Table S3. The radius, r, width of hydration shell, Δ r , number of water molecules in this shell, n, and experimental enthalpies of hydration for selected ions of Cu^{2+}, Pb^{2+} and Ag^{+} and their stability constants with some ligands

		Cu^{2+}	Pb^{2+}	Ag^{+}	H^{+}
r [pm] [3]		73	118	115	30
Δ r [pm] [3]		224	143	97	300
n [3]		9.9	6.1	3.1	12.0
ΔH_{hyd} [kJ * mol^{-1}] [4]		-2123	-1572	-483	-1103
O-containing Ligand					
Acetate	$Log\beta_1$	2.16 [a]	2.52	0.73	4.756
	$Log\beta_2$	3.20 [a]	4.0	0.64	
	$Log\beta_3$		6.4		
	$Log\beta_4$		8.5		
Citric acid (HL^{2-} Anion)	$Log\beta_1$	4.35	6.50	7.1	4.761
N-containing Ligand					

2,2'-Dipyridyl	$Log\beta_1$	8.0	3.0	3.65	4.352
		13.60		7.15	
		17.08			
Ammonia	$Log\beta_1$	4.31		3.24	9.33
	$Log\beta_2$	7.98		7.05	
	$Log\beta_3$	11.02			
	$Log\beta_4$	13.32			
Pyridine	$Log\beta_2$	4.33			4.35
	$Log\beta_4$	6.54			
S-containing Ligand					
Thourea	$Log\beta_1$		1.4	7.4	
	$Log\beta_2$		3.1	13.1	

Stability constants all value at 25° and ionic strengths approaching zero except:

[a] at 20° .[2]



5 **Figure S1.** Comparison of the imidazole-photonic film and the pyridine-based Cu-PF soaking in 0.01M pH=6.4 EDTA sodium solution to the equilibrium in pure water (pH=5.6)

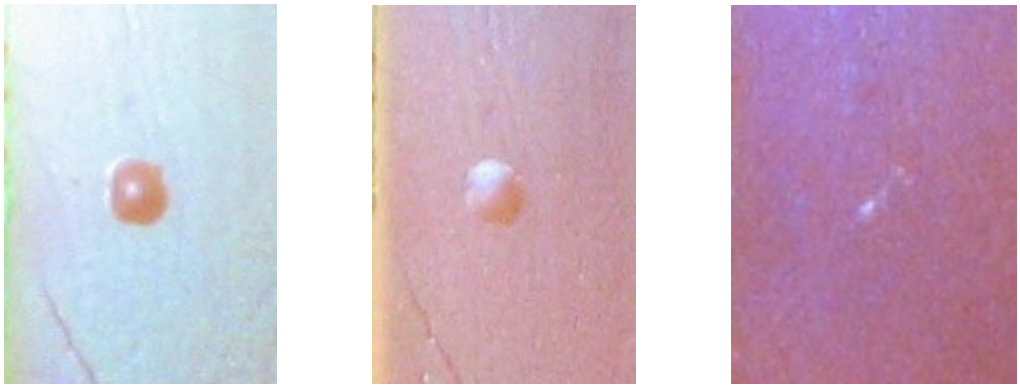
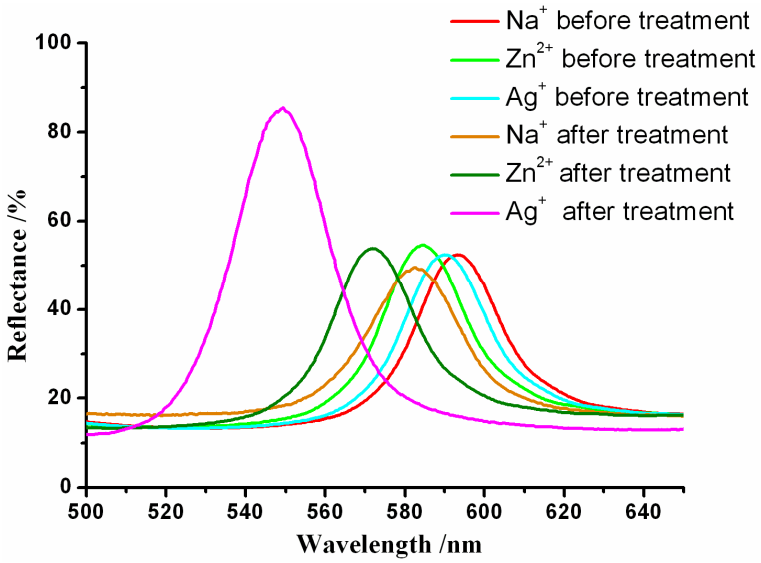


Figure S2. Enlarged picture of Pb-PF from Figure 4b to show the reversible eye on the film



5 **Figure S3.** Reflection peak wavelength shift of Ag-PF before and after TF prepolymer treatment.

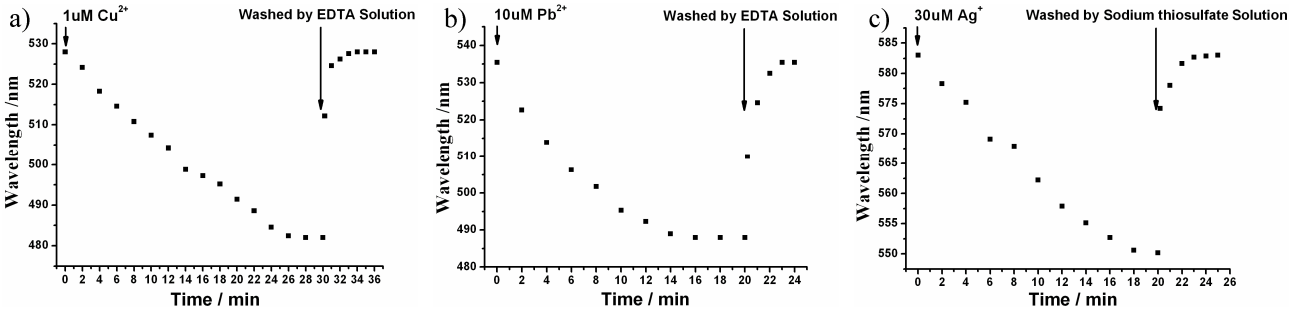
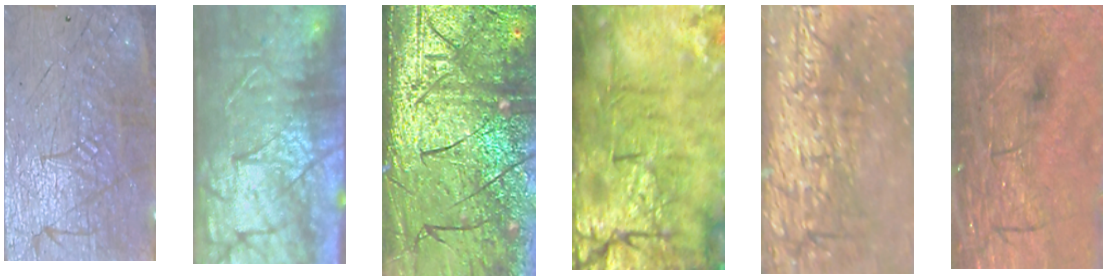
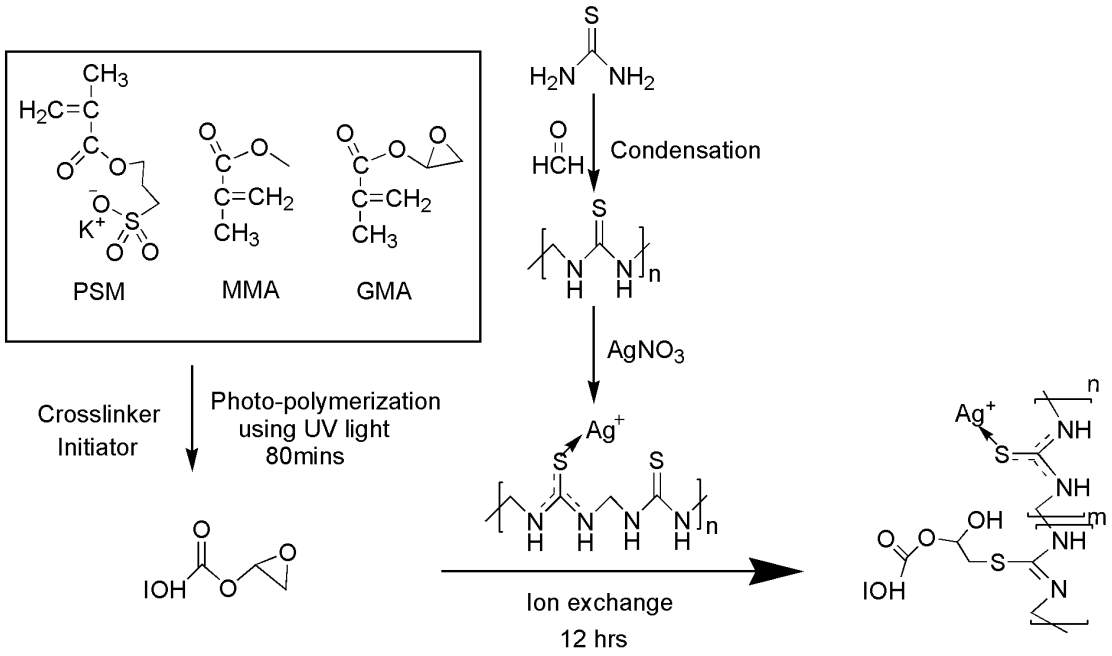


Figure S4. Time dependence of diffraction maximum upon addition of metal ions and eluant in one cycle of Figure 8, a) Cu-PF, b) Pb-PF, c) Ag-PF.



98%Ethanol	80%Ethanol 20%water	60%Ethanol 40%water	40%Ethanol 60%water	20%Ethanol 80%water	100%water
502nm	518nm	542nm	567nm	586nm	601nm

Figure S5. Effects of ethanol on the reflection peak wavelength of Cu-PF.



Scheme S1. Preparation of thiourea-formaldehyde condensate – appended inverse opal hydrogel (IOH) 5 sensor material

REFERENCES

1 R. J. Sundberg, R. B. Martin, *Chem. Rev.* 1974, **74**, 471.

2 *Lange's Handbook of Chemistry*, 15th ed., McGraw Hill, New York, 1998**.**

3 Y. J. Marcus, *J. Chem. Soc., Faraday Trans.* 1 1987, **83**, 339.

4 Y. J. Marcus, *J. Chem. Soc., Faraday Trans*. 1991, **87**, 2995.

5