Fluorescent multi-component polymer sensors for sensitive and

selective detection of Hg²⁺/Hg⁺ ions via fluorescence and colorimetry

dual mode

Kaiqi Liu^a, Luminita Marin^b, Li Xiao^a, and Xinjian Cheng^{a*}

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

Wuhan, China, 430073

^b"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi,

Romania

^{*}Corresponding author: Dr. Cheng, <u>chxj606@163.com</u>.



Figure S1. ¹H NMR spectra of small molecule compounds (a) O1, (b) BO1, (c) O2, and (d) BO2



Figure S2. (a) ¹H NMR spectra of small molecule compounds PD (b) Mass spectra of PD



Figure S3. ¹H NMR spectra of small molecule compounds (a) IBO1 and (b) IBO2



Figure S4. ¹H NMR spectra of polymer probes (a) MCP1, (b) MCP2, (c) MCP3, and (d) MCP4



Figure S5. ESI-HRMS spectrum of (a) O1 and (b) BO1



Figure S6. ESI-HRMS spectrum of (a) $\mathbf{O2}$ and (b) $\mathbf{BO2}$



Figure S7. ESI-HRMS spectrum of (a) IBO1 and (b) IBO2



Figure S8. FTIR spectra of (a) O1, BO1, IBO1, MCP1 and MCP2 and (b) O2, BO2, IBO2,

MCP3 and MCP4



Figure S9. The mechanism of PET



lake water Fe³⁺ Fe²⁺ Ni²⁺ Ba²⁺ Pb²⁺ Ag⁺ Zn²⁺Hg²⁺ H₂O Hg⁺ Cu²⁺ Mg²⁺ Na⁺ Cr³⁺ Cd²⁺ Al³⁺ Co²⁺ Ca²⁺ Mg²⁺ K⁺

Figure S10. (a) photograph of MCP1 with heavy metal ion in EtOH/H₂O under UV light. (b)



photograph of MCP1 with heavy metal ion in EtOH/H₂O under natural light.

Figure S11. Fluorescence emission spectra of macromolecular probes (1 µM) in EtOH/H₂O (1:1,

rt) (a) MCP1 and MCP2 ($\lambda ex = 440 \text{ nm}$), (b) MCP3 and MCP4 ($\lambda ex = 440 \text{ nm}$).



Figure S12. (a) photograph of MCP3 with heavy metal ion in water under natural light. (b)

photograph of MCP4 with heavy metal ion in water under natural light.



Figure S13. (a) photograph of MCP1 with different concentrations of Hg⁺ in EtOH/H₂O under UV light. (b) photograph of MCP1 with different concentrations of Hg⁺ in EtOH/H₂O under natural light. (c) photograph of MCP1 with different concentrations of Hg²⁺ in EtOH/H₂O under UV light. (d) photograph of MCP1 with different concentrations of Hg²⁺ in EtOH/H₂O under natural light. (e) photograph of MCP2 with different concentrations of Hg⁺ in EtOH/H₂O under UV light. (f) photograph of MCP2 with different concentrations of Hg⁺ in EtOH/H₂O under UV light. (g) photograph of MCP2 with different concentrations of Hg⁺ in EtOH/H₂O under natural light. (g) photograph of MCP2 with different concentrations of Hg²⁺ in EtOH/H₂O under UV light. (h) photograph of MCP2 with different concentrations of Hg²⁺ in EtOH/H₂O under

natural light.



Figure S14. (a) Concentration effect of MCP3 on Hg⁺. (b) Concentration effect of MCP3 on Hg²⁺.

(c) Concentration-dependent fluorescence signaling of a Hg^+ by MCP3, and (d) Hg^{2+} by MCP3



Figure S15. (a) photograph of MCP3 with different concentrations of Hg⁺ in water under natural



light. (b) photograph of MCP3 with different concentrations of Hg^{2+} in water under natural light.

Figure S16. (a) photograph of **MCP4** with different concentrations of Hg⁺ in water under natural light. (b) photograph of **MCP4** with different concentrations of Hg²⁺ in water under natural light.

Table S1. Comparison of the basic properties of the reported probe and the probe synthesized in

this article				
Sensor	Selectivity	LOD	Analytical	Reference
			applications	
1-CN	Good (Hg ²⁺)	0.8µM	Cell image	[1]
9AnPD	Effective (Hg ²⁺)	5μΜ		[2]
BAN	Remarkable (Hg ²⁺)	0.00173 μM	Living HeLa	[3]
			cells	
probe 1	Sensitive (Hg ²⁺)	0.2µM	Living cells	[4]
L	High (Hg ²⁺)	1.1µM	Living cell	[5]
			imaging	
PTS	Sensitive (Hg ²⁺)	0.23µM		[6]
RFP3	Excellent	0.012µM	HL-7702	[7]
	(Hg^{2+}/Cu^{2+})		cells	
P-3	High (Hg ²⁺)	4.8µM		[8]
MCP2	Sensitive (Hg ²⁺ /Hg ⁺)	0.32/0.42µM	Lake water	This work



Figure S17. Benesi–Hilderbrand plot of (a) MCP1+Hg⁺, (b) MCP1+Hg²⁺, (c)



MCP2+Hg⁺, and (d) MCP2+Hg²⁺

Figure S18. Benesi–Hilderbrand plot of (a) MCP3+Hg⁺, (b) MCP3+Hg²⁺, (c)



Figure S19. The fluorescence intensity of the polymer solution changes with the concentration of Hg²⁺/Hg⁺ (a) **MCP1**+Hg⁺(1 μ M, pH = 7.0, rt); (b)**MCP1**+Hg²⁺ (1 μ M, pH = 7.0, rt); (c)**MCP2**+Hg⁺ (1 μ M, pH = 7.0, rt); (d)**MCP2**+Hg²⁺ (1 μ M, pH = 7.0, rt)



Figure S20. Absorbance of probes (10 μ M) with other metal ions (100 μ M) and albumin (3.6 mg/mL) in aqueous solution. The black bars represent the addition of different ions to the solution of correspond sensor. The red bars represent the subsequent addition of Hg²⁺/Hg⁺ the solution.



Figure S21. The fluorescence emission spectrum of sensor in EtOH/H₂O and EtOH/natural lake water. (a) **MCP1**, (b) **MCP2**. UV absorption spectra of sensor in water and natural lake water. (c)

MCP3, (d) MCP4



Figure S22. (a) ¹H NMR of **MCP1** in DMSO-d6, (b) ¹H NMR of **MCP1** and equimolar amount of Hg⁺ in DMSO-d6. (c) ¹H NMR of **MCP1** and equimolar amount of Hg²⁺ in DMSO-d6.

References

[1] J. Ding, H. Li, C. Wang, J. Yang, Y. Xie, Q. Peng, Q. Li, Z. Li, "Turn-On" Fluorescent Probe for Mercury(II): High Selectivity and Sensitivity and New Design Approach by the Adjustment of the pi-Bridge, ACS Appl Mater Interfaces 7(21) (2015) 11369-

76.http://dx.doi.org/10.1021/acsami.5b01800

[2] Y. Jia, Y. Pan, H. Wang, R. Chen, H. Wang, X. Cheng, Highly selective and sensitive polymers with fluorescent side groups for the detection of Hg 2+ ion, Materials Chemistry and Physics 196 (2017) 262-269.<u>http://dx.doi.org/10.1016/j.matchemphys.2017.05.001</u>

[3] H. Xiao, J. Li, K. Wu, G. Yin, Y. Quan, R. Wang, A turn-on BODIPY-based fluorescent probe for Hg(II) and its biological applications, Sensors and Actuators B: Chemical 213 (2015) 343-350.http://dx.doi.org/10.1016/j.snb.2015.02.105

[4] Z. Zhu, H. Ding, Y. Wang, C. Fan, Y. Tu, G. Liu, S. Pu, A ratiometric and colorimetric fluorescent probe for the detection of mercury ion based on rhodamine and quinoline– benzothiazole conjugated dyad, Journal of Photochemistry and Photobiology A: Chemistry 400 (2020).<u>http://dx.doi.org/10.1016/j.jphotochem.2020.112657</u>

[5] W. Feng, Q. Xia, H. Zhou, Y. Ni, L. Wang, S. Jing, L. Li, W. Ji, A fluorescent probe based upon anthrancene-dopamine thioether for imaging Hg(2+) ions in living cells, Talanta 167 (2017) 681-687.<u>http://dx.doi.org/10.1016/j.talanta.2017.03.012</u>

[6] Y. Shan, W. Yao, Z. Liang, L. Zhu, S. Yang, Z. Ruan, Reaction-based AIEE-active conjugated polymer as fluorescent turn on probe for mercury ions with good sensing performance, Dyes and Pigments 156 (2018) 1-7.<u>http://dx.doi.org/10.1016/j.dyepig.2018.03.060</u>

[7] M. Wang, F. Yan, Y. Zou, L. Chen, N. Yang, X. Zhou, Recognition of Cu2+ and Hg2+ in physiological conditions by a new rhodamine based dual channel fluorescent probe, Sensors and Actuators B: Chemical 192 (2014) 512-521.<u>http://dx.doi.org/10.1016/j.snb.2013.11.031</u>

[8] Y. Lei, F. Ma, Y. Tian, Q. Niu, H. Mi, I. Nurulla, W. Shi, Fluorene-based conjugated polymer with tethered thymines: click postpolymerization synthesis and optical response to mercury(II), Journal of Applied Polymer Science 129(4) (2013) 1763-

1772.<u>http://dx.doi.org/10.1002/app.38817</u>