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Electronic Supplementary Information

Super-assembled Silica Nanoprobes for Intracellular Zn Ion Sensing and Reperfusion Injury Treatment through in-situ MOF Crystallization

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This ESI includes:

Figure S1. The synthesis process of probe PZn through a mild Schiff base reaction.

Figure S2. ^1H NMR spectrum of probe PZn.

Figure S3. TEM image, SEM image and size distribution of P@MSN@ZIF8.

Figure S4. Fluorescence spectra and visual fluorescence color of PZn treated with various metal ions.

Figure S5. Fluorescence intensity of PZn at different stoichiometric ratios of Zn^{2+} and PZn.

Figure S6. The relative fluorescence intensity of the PZn after adding 2MI at different concentration ratios and various times.

Figure S7. In vitro cytotoxicity assay of 2MI-P@MSN on SH-SY5Y cells.

Figure S8. The cell viability of SH-SY5Y cells incubated with P@MSN and 2MI-P@MSN and treated with OGD/R for 6 hours.

Table S1. Surface properties of MSN-NH₂ and 2MI-P@MSN samples.

Table S2. Comparison with the recent work on Zn^{2+} probe.

References

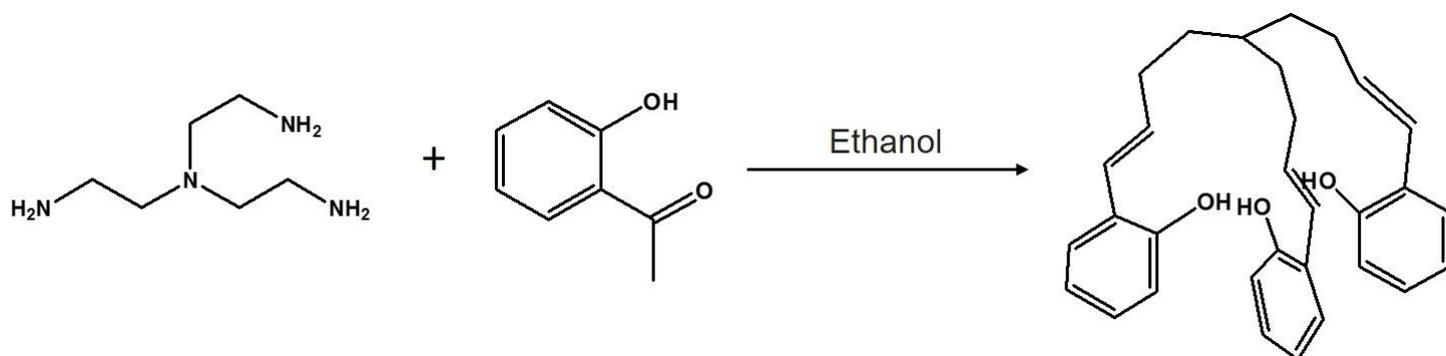


Figure S1. The synthesis process of PZn probe through a mild Schiff base reaction.

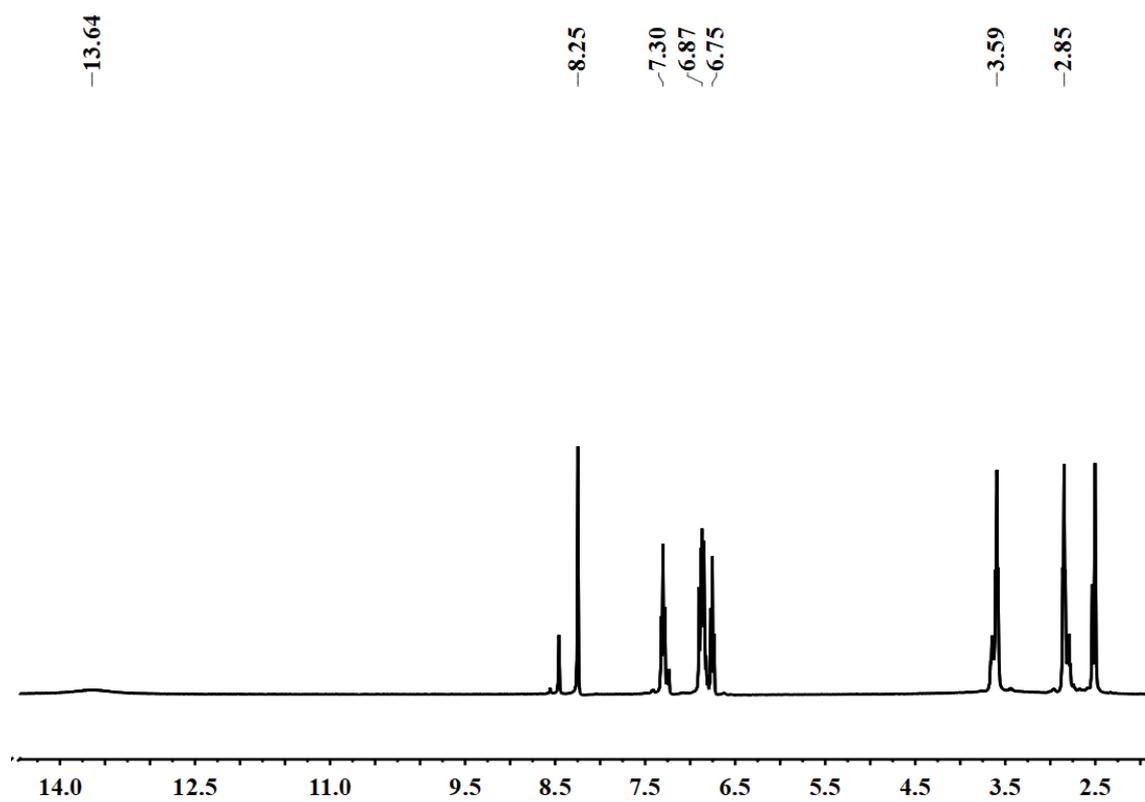


Figure S2. ^1H NMR spectrum of PZn probe.

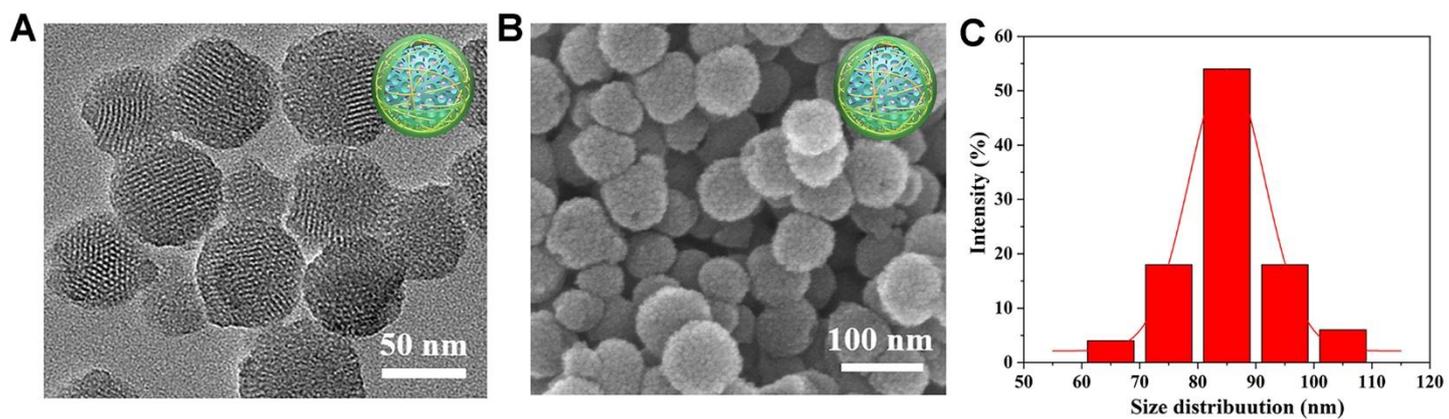


Figure S3. (A) TEM image of P@MSN@ZIF8 incubated with zinc ion for 3 hours. (B) SEM image of P@MSN@ZIF8. (C) Size distribution of P@MSN@ZIF8.

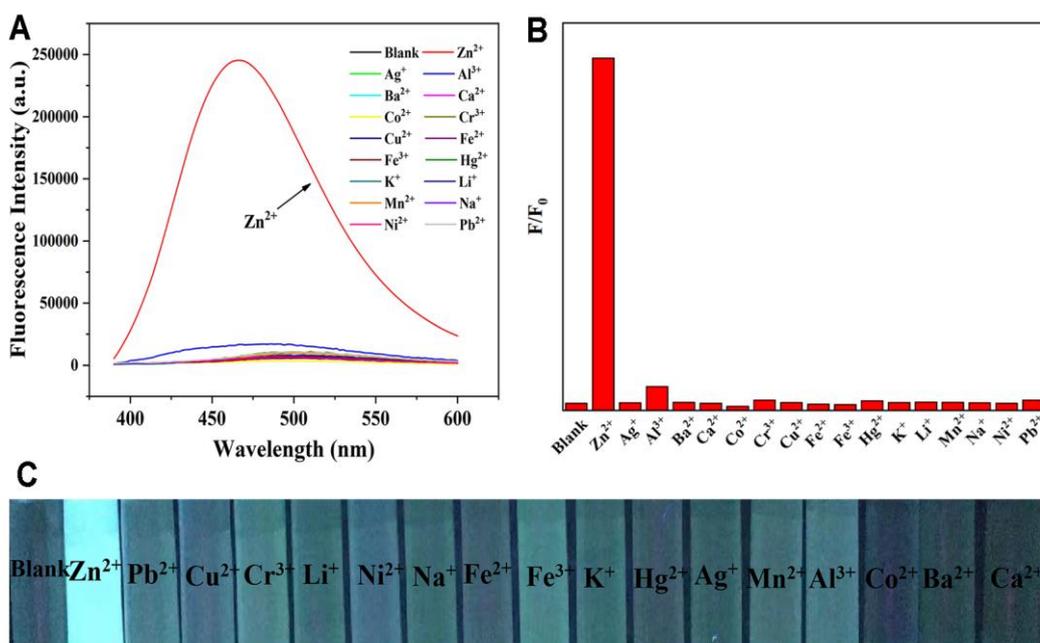


Figure S4. (A) Fluorescence spectra of PZn treated with various metal ions (Zn²⁺, Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Fe²⁺, Hg²⁺, K⁺, Li⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺) and blank group. (B) Fluorescence ratio of PZn at 466 nm treated with multiple metal ions. F₀ was the fluorescence intensity in Zn²⁺ solution and F was the fluorescence emission intensity of the PZn in various metal ions solution, respectively. (C) The visual fluorescence color of PZn under ultraviolet light after the addition of various metal ions.

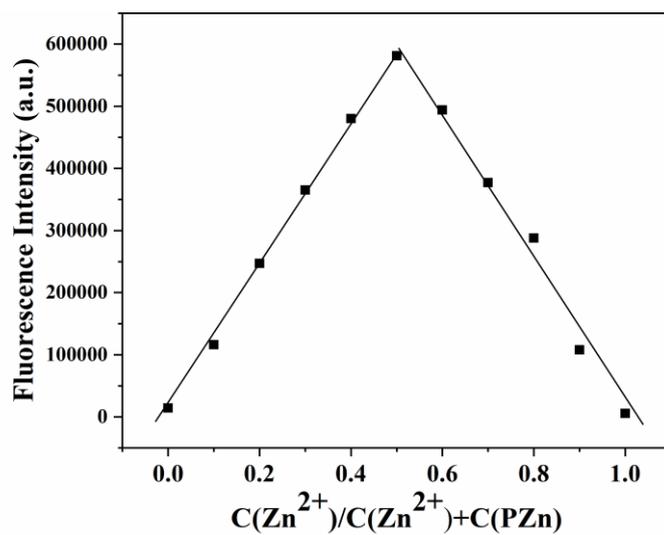


Figure S5. Fluorescence intensity of PZn at different stoichiometric ratios of Zn^{2+} and PZn. The total concentration was $1 \times 10^{-4} \text{ M}$.

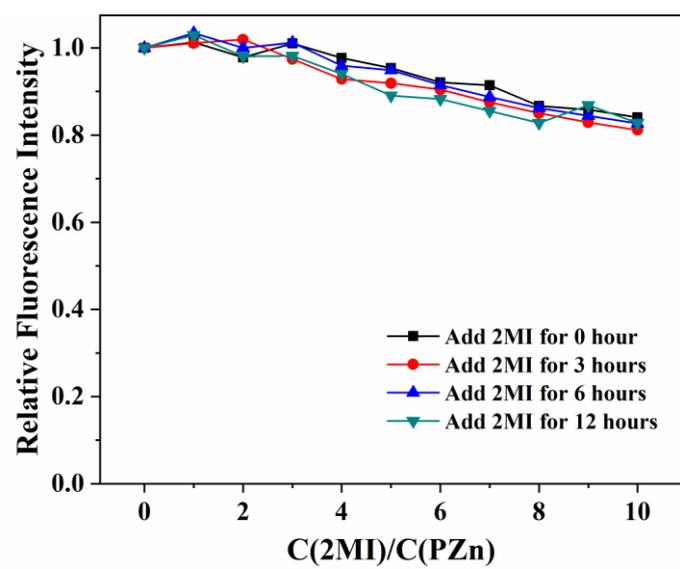


Figure S6. The relative fluorescence intensity of the PZn after adding 2MI at different concentration ratios and various times.

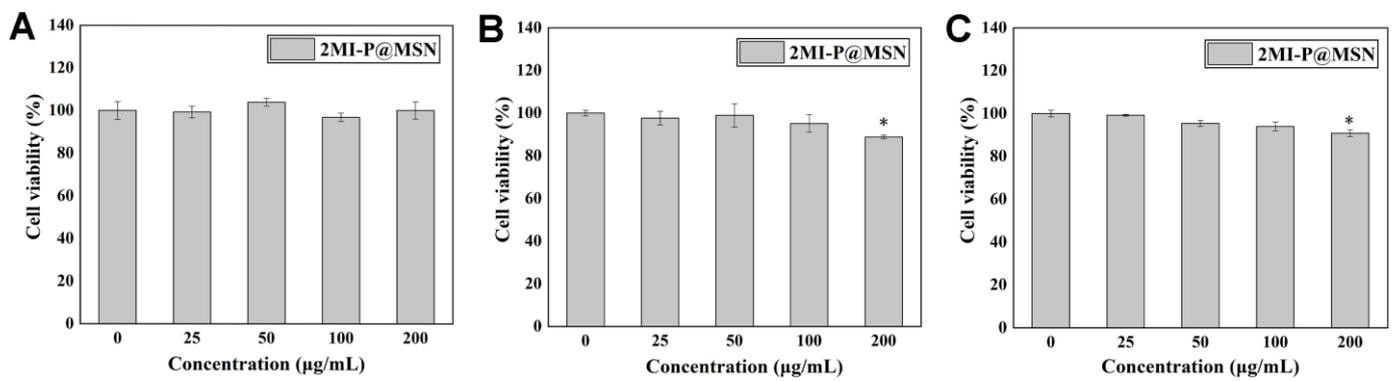


Figure S7. In vitro cytotoxicity assay of 2MI-P@MSN on SH-SY5Y cells. (A-C) The cell viability of SH-SY5Y cells incubated with various concentrations of 2MI-P@MSN for 3, 6, 12 hours, respectively. * $P < 0.05$ and ** $P < 0.01$.

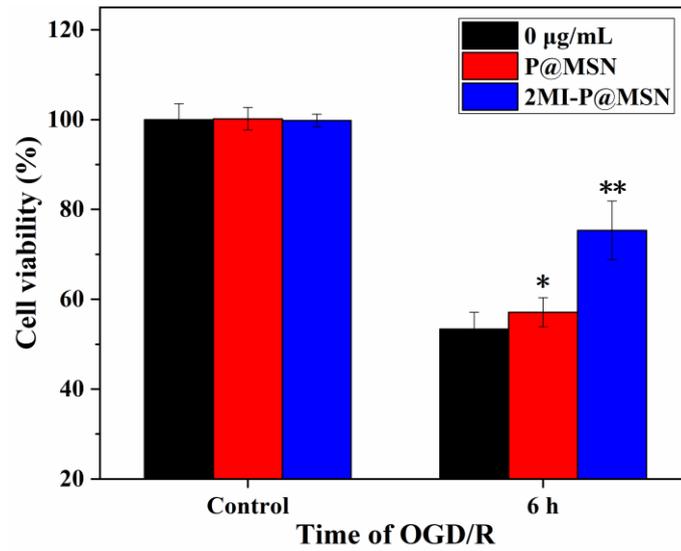


Figure S8. The cell viability of SH-SY5Y cells incubated with P@MSN and 2MI-P@MSN and treated with OGD/R for 6 hours. The control was the cell viability of SH-SY5Y cells incubated with 0 and 25 µg/mL of P@MSN and 2MI-P@MSN. The 6 h was the cell viability of SH-SY5Y cells treated with OGD 3 hours and reperfusion for 6 hours. * $P < 0.05$ and ** $P < 0.01$.

	MSN-NH ₂	2MI-P@MSN
<i>S_{BET}</i> (m ² /g)	897.398	267.023
<i>V_t</i> (cm ³ /g)	0.947	0.632
<i>D_{BJH}</i> (nm)	2.11	1.96

Table S1. Surface properties of MSN-NH₂ and 2MI-P@MSN samples. The *S_{BET}* was the Brunauer–Emmett–Teller (BET) surface area, *V_t* was the pore volume, *D_{BJH}* was the Barrett-Joyner-Halenda (BJH) pore size distribution.

No.	Emission Wavelength	Detection Limit (LOD)	Stoichiometric Ratio	Solvent	Function	Reference
1	410 nm	5.2×10^{-7} M	1:3	DMF/H ₂ O (6:4, v/v)	Zn ²⁺ detection	[S1]
2	450 nm	3.5×10^{-7} M	1:1	Ethanol	Zn ²⁺ detection	[S2]
3	365 nm、555 nm	5.0×10^{-8} M	1:1	Ethanol	Zn ²⁺ detection	[S3]
4	405 nm	4.2×10^{-7} M	1:1	HEPES buffer with 0.01% Triton X-100	Zn ²⁺ detection	[S4]
5	560 nm	1.7×10^{-8} M	1:1	CH ₃ CN/H ₂ O (1:1, v/v)	Zn ²⁺ detection	[S5]
6	535 nm	3.8×10^{-8} M	1:1	MeOH/H ₂ O (4:1, v/v)	Zn ²⁺ detection	[S6]
7	466 nm	1.6×10^{-7} M	1:1	H ₂ O	Zn ²⁺ detection, cell protection	This work

Table S2. Comparison with the recent work on Zn²⁺ probe.

The performance of the Zn²⁺ ion probe proposed in this work was compared with other reported methods in literatures. According to Table S2, relatively low LOD was achieved by 2MI-P@MSN in this work. Moreover, 2MI-P@MSN showed high selectivity and sensitivity towards detection of Zn²⁺ ion in aqueous solutions and living cells. In addition to intracellular zinc ion imaging, 2MI-P@MSN also protected cells from reperfusion injury. In summary, the proposed method in this work realized the integration of detection effects and protection effects into a multi-functional material framework and obtained satisfactory results.

References

- [S1] L. Z. Liu, L. Wang, M. Yu, Q. Zhao, Y. Zhang, Y. X. Sun and W. K. Dong, *Spectrochim Acta A Mol Biomol Spectrosc* **2019**, 222, 117209.
- [S2] L. Fan, J. C. Qin, C. R. Li and Z. Y. Yang, *Spectrochim Acta A Mol Biomol Spectrosc* **2020**, 236, 118347.
- [S3] H. Diao, L. Guo, W. Liu and L. Feng, *Spectrochim Acta A Mol Biomol Spectrosc* **2018**, 196, 274-280.
- [S4] G. Zhang, Y. Zhao, B. Peng, Z. Li, C. Xu, Y. Liu, C. Zhang, N. H. Voelcker, L. Li and W. Huang, *J Mater Chem B* **2019**, 7, 2252-2260.
- [S5] H. Fang, P. C. Huang and F. Y. Wu, *Spectrochim Acta A Mol Biomol Spectrosc* **2019**, 214, 233-238.
- [S6] J. Fu, Y. Chang, B. Li, X. Wang, X. Xie and K. Xu, *Spectrochim Acta A Mol Biomol Spectrosc* **2020**, 225, 117493.