Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Porphyrinic MOFs for reversible fluorescent and colorimetric sensing of mercury (II) ions in aqueous-phase

Jian Yang, Zhe Wang, Yongsheng Li, Qixin Zhuang, Wenru Zhao and Jinlou Gu*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Fax: +86-21-64250740; Tel: +86-21-64252599

E-mails: jinlougu@ecust.edu.cn

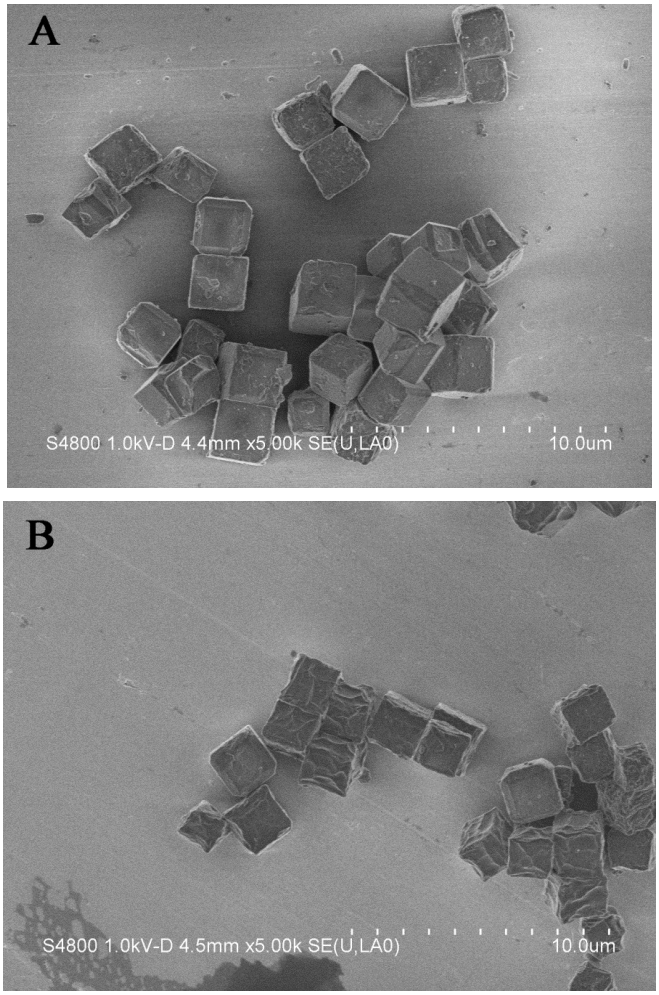

Fig. S1 Scanning electron microscopy (SEM) images of (A) the as-synthesized PCN-224 and (B) PCN-224-KI particles regenerated by KI solution.

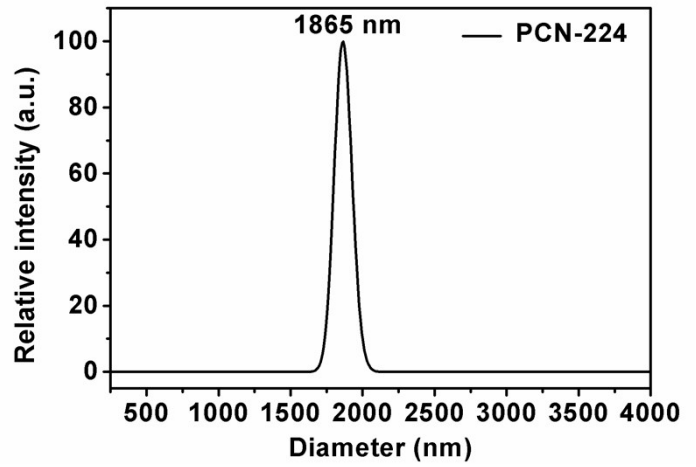

Fig. S2 Typical DLS profile of PCN-224 particles measured in aqueous solution.

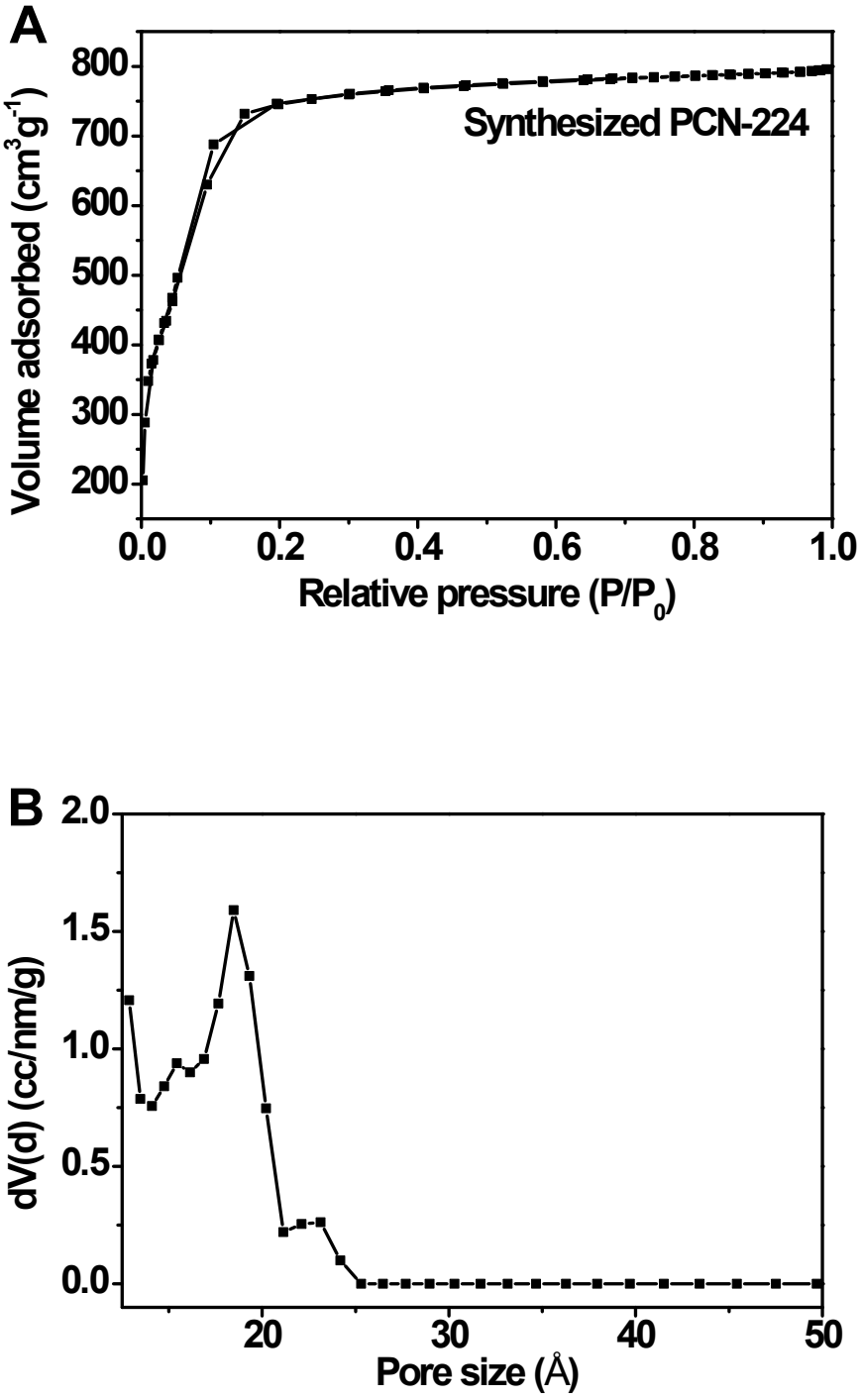

Fig. S3 (A) N_2 sorption isotherm at 77 K for the as-synthesized PCN-224 particles and (B) is the corresponding pore size distribution calculated by the DFT method.

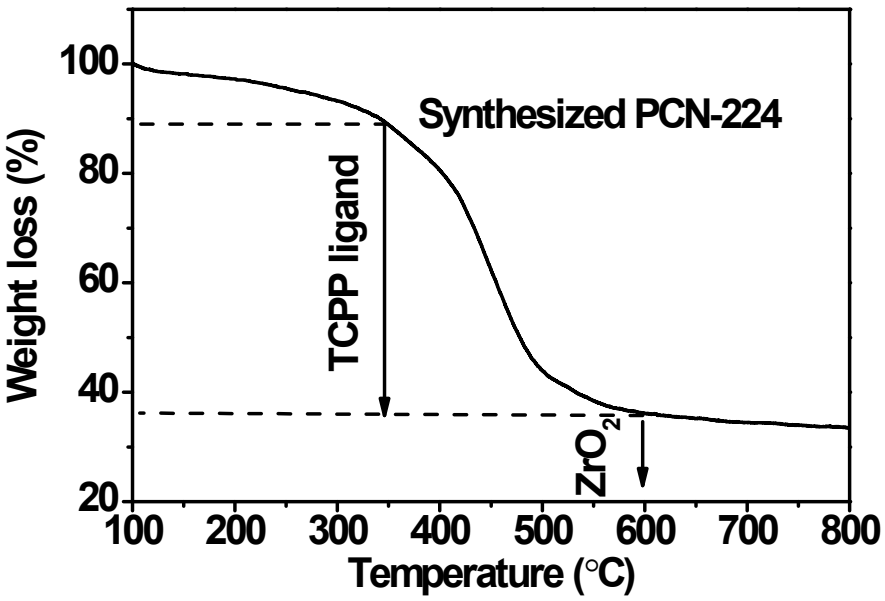

Fig. S4 TGA profile for the as-synthesized PCN-224 particles recorded under air flow.

The calculation for the limit of detection (LOD)

$$\text{Detection Limit} = 3\sigma/\text{slope}$$

$$= (3 \times 0.17)/81.1 \times 1000$$

$$= 6 \text{ nM}$$

Multiple number of PL spectra (n = 10) were recorded for the blank sample of PCN-224 suspension. Sample standard deviation σ for the blank probe without the addition of Hg^{2+} was calculated to be 0.17.

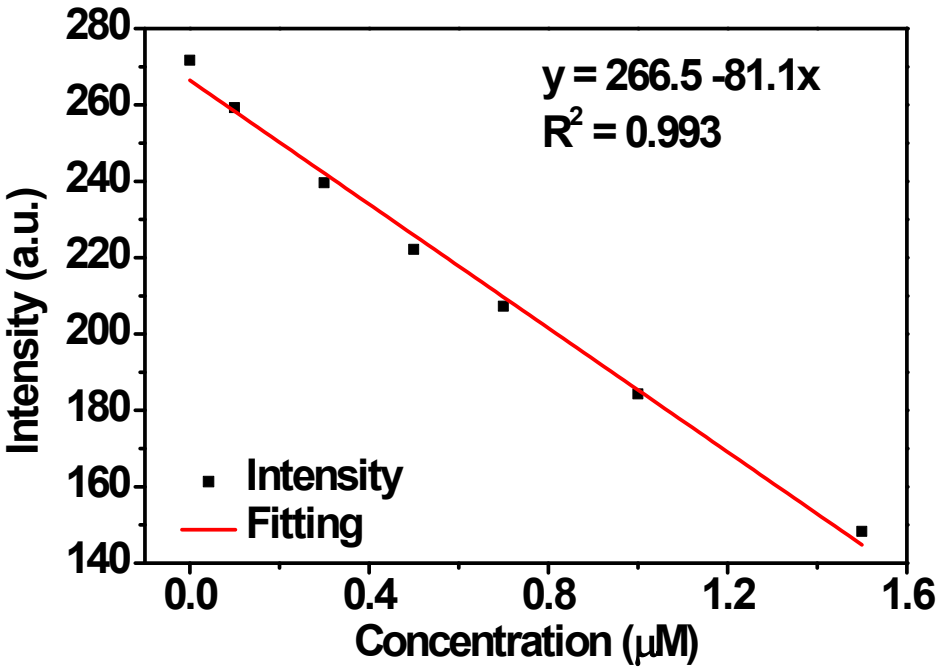

Fig. S5 Relation of fluorescence intensity against Hg^{2+} added into PCN-224 suspension and their linear fitting curve for the estimation of LOD.

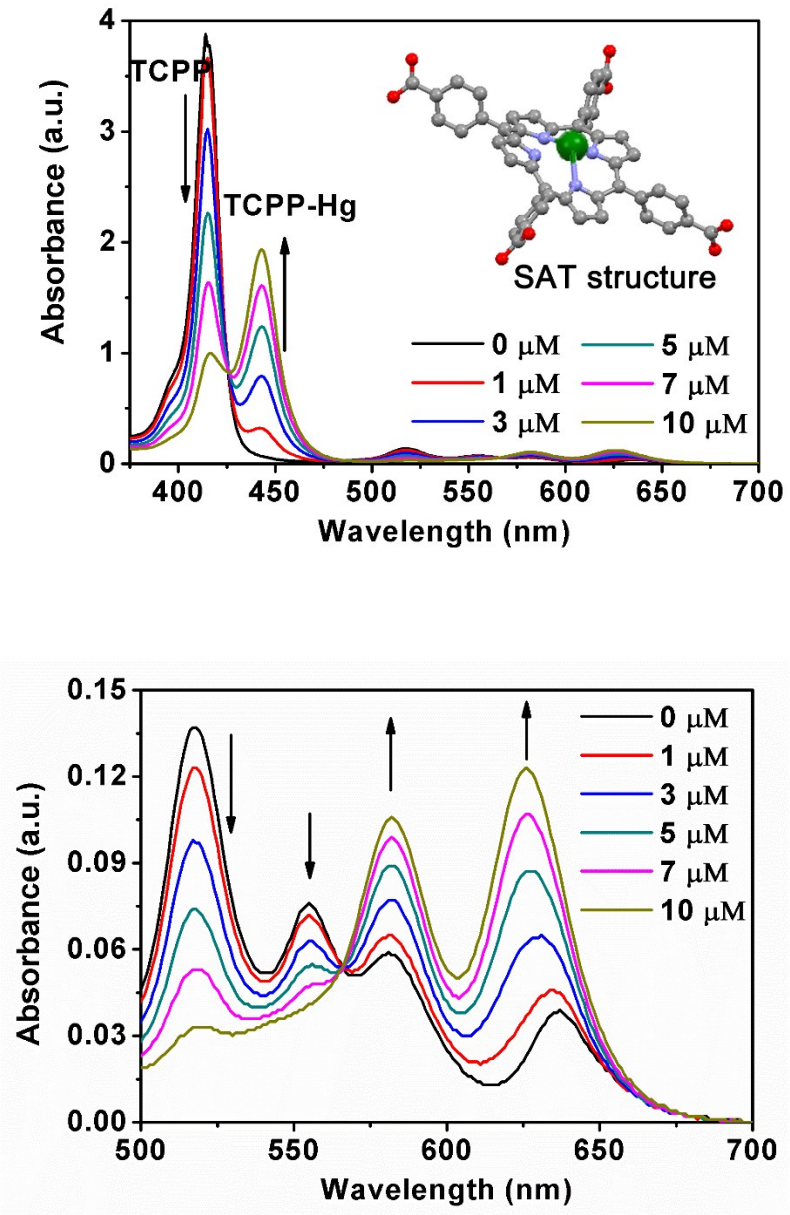

Fig. S6 The evolvement of UV-Vis spectra of (A) the Soret band and (B) the enlargement of Q bands for free TCPP molecules (10 mg L^{-1}) in DMF/HEPES buffer solution (v/v = 1:1, pH = 7) upon the addition of various concentrations of Hg^{2+}. In the inset, schematic representations of the interaction mechanisms between the porphyrin molecule and Hg^{2+} ions in the PCN-224 probe, which is a "sitting-atop" (SAT) structure.

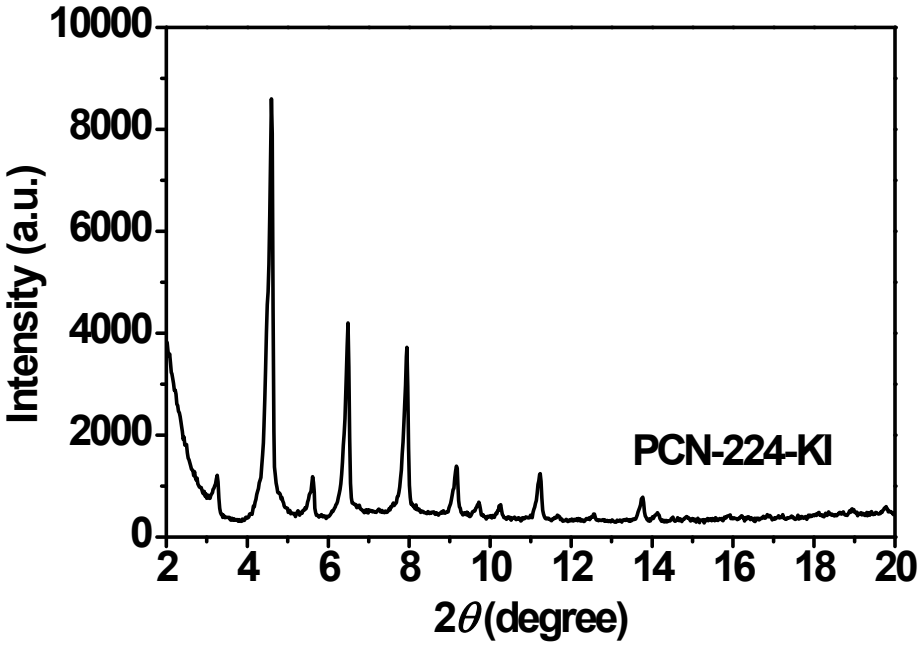

Fig. S7 Powder XRD patterns of the PCN-224-KI particles regenerated by KI solution.

Table S1. The Comparison of Sensing Features between the Current PCN-224 Sensor and Other Reported Probes for the Detection of Hg^{2+}.

Probe	Material	Detection range (μM)	LOD (nM)	Response Time	Regeneration	References
MOF-based sensors	$\{[Eu_2(bqdc)_3(H_2O)(DMF)_3]\cdot 0.5DMF\cdot H_2O\}_n$	10-1000	10	4 h	—	1
	$TbL_{1.5}(H_2O)_2]\cdot H_2O$	1-1000	—	—	EDTA	2
	$Zr_6O_4(OH)_4(BDC)_6$	0.001-0.5	52	10 s	ClO_4^-	3
	$\{[Cd_{1.5}(C_{18}H_{10}O_{10})]\cdot(H_3O)(H_2O)_3\}_n$	4-25	2	15s	—	4
	UiO-66-NH_2@DNA	0.1-10	17.6	—	—	5
	COF-LZU8	0.33-33.3	125	Real-time	Na_2S	6
Other porphyrin-based sensors	H_2TPP	0.04-450	40	4 min	3-MPA	7
	TDMAPP	0.04-4	8	—	HCl	8
	naphthalimide-porphyrin	0.1-50	20	2 min	EDTA	9
	DTPP	0.5-310	—	9 min	HCl	10
	MTHNP	0.005-12.5	3	3 min	buffer[a]	11
	cationic porphyrin[b]	0.0001-1	0.1	—	—	12
	TPPS@SBA-15	0.025-0.5	17.5	4 min	—	13
PCN-224 sensor	**$Zr_6O_4(OH)_4(TCPP)_{1.5}$**	**0.1-10**	**6**	**2 min**	**KI**	**This work**

[a] *the blank phosphate buffer of pH 7.5*

[b] *the cationic 5,15-(p-(9,9-bis(6-trimethylammoniumhexyl)fluorenylethynyl)phenyl)-porphyrin tetrabromide*

References

1 Y.-M. Zhu, C.-H. Zeng, T.-S. Chu, H.-M. Wang, Y.-Y. Yang, Y.-X. Tong, C.-Y. Su and W.-T. Wong, *J. Mater. Chem. A*, 2013, **1**, 11312–11319.

2 H.-M. Wang, Y.-Y. Yang, C.-H. Zeng, T.-S. Chu, Y.-M. Zhu and S. W. Ng, *Photochem. Photobiol. Sci*., 2013, **12**, 1700–1706.

3 A. Shahat, H. M.A. Hassana and H. M.E. Azzazy, *Anal. Chim. Acta*, 2013, **793**, 90–98.

4 P. Wu, Y. Liu, Y. Liu, J. Wang, Y. Li, W. Liu and J. Wang, *Inorg. Chem*., 2015, **54**, 11046−11048.

5 L.-L. Wu, Z. Wang, S,-N, Zhao, X. Meng, X.-Z. Song, J. Feng, S.-Y. Song and H.-J. Zhang, *Chem. Eur. J*., 2016, **22**, 477 – 480.

6 S.-Y. Ding, M. Dong, Y.-W. Wang, Y.-T. Chen, H.-Z. Wang, C.-Y. Su and W. Wang, *J. Am. Chem. Soc*., 2016, **138**, 3031−3037.

7 W. Chana, R. Yang and K. Wang, *Anal. Chim. Acta*, 2001, **444**, 261–269.

8 Y. Yang, J. Jiang, G. Shen and R. Yu, *Anal. Chim. Acta*, 2009, **636**, 83–88.

9 C.-Y. Li, X.-B. Zhang, L. Qiao, Y. Zhao, C.-M. He, S.-Y. Huan, L.-M. Lu, L.-X. Jian, G.-L. Shen and R.-Q. Yu, *Anal. Chem*., 2009, **81**, 9993–10001.

10 X.-B. Zhang, C.-C. Guo, Z.-Z. Li, G.-L. Shen and R.-Q. Yu, *Anal. Chem*., 2002, **74**, 821–825.

11 M. Shamsipura, M. Sadeghi, M. Beyzavi and H. Sharghi, *Mater. Sci. Eng. C*, 2015, **48**, 424–433.

12 Z. Fang and B. Liu, *Tetrahedron Lett*., 2008, **49**, 2311–2315.

13 T. Balaji, M. Sasidharan and H. Matsunaga, *Analyst*, 2005, **130**, 1162–1167.