

Electronic Supporting Information

**A Highly Stable Indium Phosphonocarboxylate Framework
as a Multifunctional Sensor for Cu²⁺ and Methylviologen
Ions**

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Table S1 Selected bond lengths (Å) and angles (°) for **InPCF-1**.

| | | | |
|---------------------|-----------|-------------------|-----------|
| In(1)-O(2) | 2.072(6) | O(1)-In(1)#8 | 2.141(5) |
| In(1)-O(3) | 2.119(7) | In(1)-O(5) | 2.254(7) |
| In(1)-O(1)#1 | 2.141(5) | In(1)-O(6) | 2.302(7) |
| In(1)-O(1)#2 | 2.141(5) | P(1)-O(1) | 1.528(5) |
| P(1)-O(2) | 1.527(7) | P(1)-O(1)#3 | 1.528(5) |
| O(3)-C(14) | 1.259(14) | O(4)-C(14) | 1.245(14) |
| O(5)-C(13) | 1.261(12) | O(6)-C(13) | 1.255(12) |
| O(2)-In(1)-O(1)#1 | 99.27(12) | O(2)-In(1)-O(3) | 84.5(3) |
| O(2)-In(1)-O(1)#2 | 99.27(12) | O(3)-In(1)-O(1)#1 | 87.90(13) |
| O(1)#1-In(1)-O(1)#2 | 160.5(2) | O(3)-In(1)-O(1)#2 | 87.90(13) |
| O(3)-In(1)-O(5) | 129.2(3) | O(2)-In(1)-O(5) | 146.4(2) |
| O(1)#2-In(1)-O(5) | 83.97(12) | O(1)#1-In(1)-O(5) | 83.97(12) |
| O(3)-In(1)-O(6) | 173.7(3) | O(2)-In(1)-O(6) | 89.3(2) |
| O(1)#2-In(1)-O(6) | 93.13(12) | O(1)#1-In(1)-O(6) | 93.13(12) |

Symmetry transformations used to generate equivalent atoms: #1 $-y+1/2, -x+1/2, -z+3/2$;
#2 $-y+1/2, -x+1/2, z+1/2$; #3 $x, y, -z+2$; #4 $-y+1, x, z$; #5 $y, -x, -z+2$; #6 $-y, x, z$; #7 $y, -x+1, -z+2$ #8 $-y+1/2, -x+1/2, z-1/2$

Table S2 Hydrogen bonds for InPCF-1^a.

| D-H...A | d(D-H) / Å | d(H...A) / Å | d(D...A) / Å | <DHA / ° |
|---------------------|------------|--------------|--------------|----------|
| O(8)-H(8B)...O(1) | 0.85 | 2.16 | 2.991(18) | 165.4 |
| O(9)-H(9A)...O(4)#8 | 0.85 | 1.93 | 2.78(3) | 179.0 |

^aSymmetry code: #8 -y+1/2, -x+1/2, z-1/2

Table S3 Comparison of some MOFs for sensing Cu²⁺ ion at room temperature

| MOFs | K_{sv}/M^{-1} | Active sites | The charge of frameworks | Pore size |
|---|-----------------|--------------------------------------|--------------------------|---|
| InPCF-1 | 1840.1 | Uncoordinated carbonyl oxygen sites | anion | $7.19 \times 7.19 \text{ \AA}^2$ |
| [Eu(pdc)] _n ¹ | 89.4 | Uncoordinated pyridyl nitrogen sites | neutral | $6.3 \times 8.5 \text{ \AA}^2$ |
| [Mg(DHT)] _n ² | 170.2 | Uncoordinated hydroxyl oxygen sites | neutral | $5.3 \times 5.5 \text{ \AA}^2$ |
| {[Tb ₄ (μ ₃ -OH) ₄ (BPDC) ₃ (BPDCA) _{0.5} (H ₂ O) ₆]-ClO ₄] _n ³ | 344.7 | Uncoordinated pyridyl nitrogen sites | cationic | $4.5 \times 5.5 \text{ \AA}^2$ |
| [Eu ₂ (FMA) ₂ (OX)(H ₂ O) ₄] _n ⁴ | 528.7 | Carboxylate oxygen sites | neutral | $4.0 \times 5.0 \text{ \AA}^2$ $3.8 \times 3.8 \text{ \AA}^2$ |
| [Eu ₃ (L) ₂ (HCOO) ₂ (DMF) ₂ (H ₂ O)] [H ₂ N(Me) ₂] _n ⁵ | 2350 | Uncoordinated pyridyl nitrogen sites | anion | $4.5 \times 5.5 \text{ \AA}^2$ (window) 11 \AA (cage) |

References

- 1 B. L. Chen, L. B. Wang, Y. Q. Xiao, F. R. Fronczek, M. Xue, Y. J. Cui and G. D. Qian, *Angew. Chem. Int. Ed.* **2009**, *48*, 500–503.
- 2 K. Jayaramulu, R. P. Narayanan, S. J. George and T. K. Maji, *Inorg. Chem.* **2012**, *51*, 10089–10091.
- 3 Y. Q. Xiao, Y. J. Cui, Q. Zheng, S. C. Xiang, G. D. Qian and B. L. Chen, *Chem. Commun.* **2010**, *46*, 5503–5505.
- 4 J. M. Zhou, W. Shi, H. M. Li, H. Li and P. Cheng, *J. Phys. Chem. C* **2014**, *118*, 416–426.
- 5 B. Liu, W. P. Wu, L. Hou and Y. Y. Wang, *Chem. Commun.* **2014**, *50*, 8731–8734.

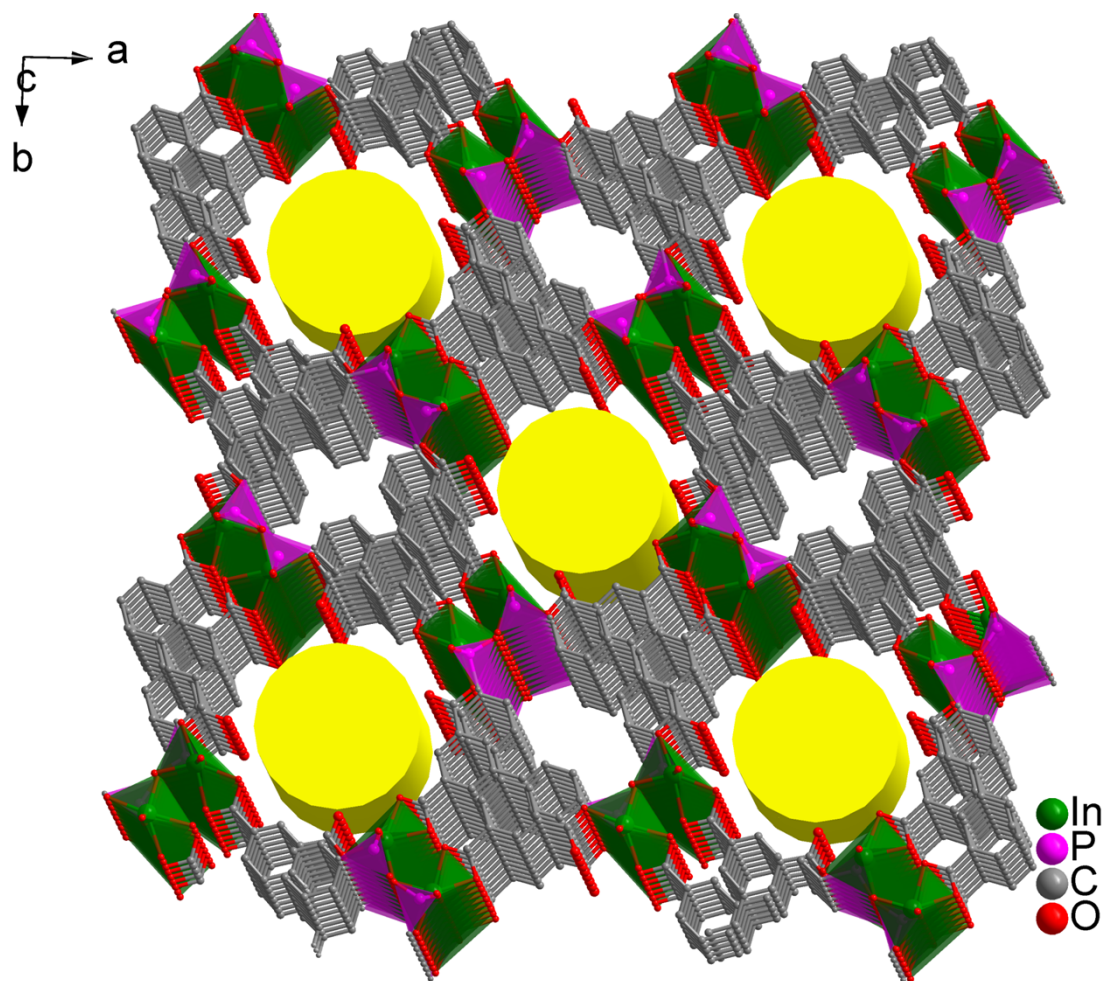


Figure S1 Packing view of InPCF-1 (Water and hydrogen atoms is omitted for clarity yellow columns are added to highlight the 1-D channels).

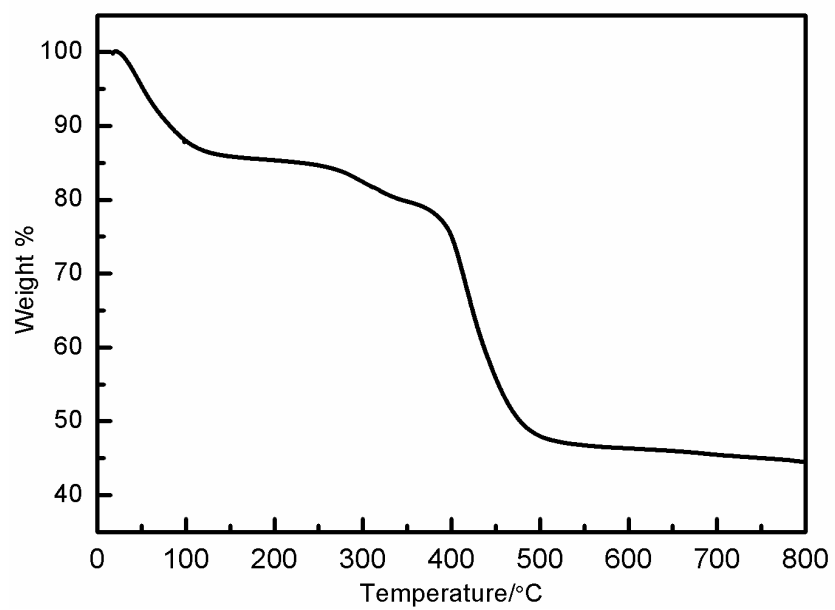


Figure S2 TGA curve of as-synthesized **InPCF-1**.

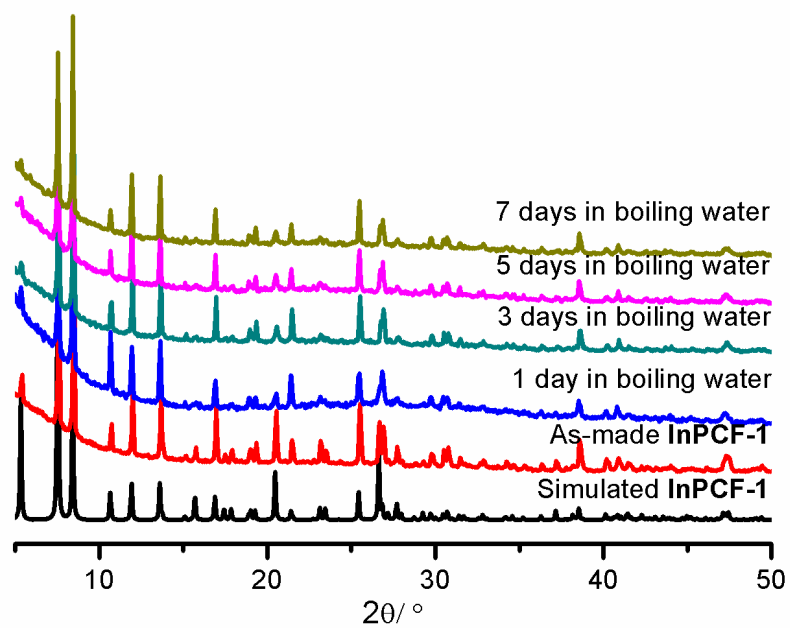


Figure S3 The PXRD patterns for **InPCF-1** in boiling water for up to 7 days.

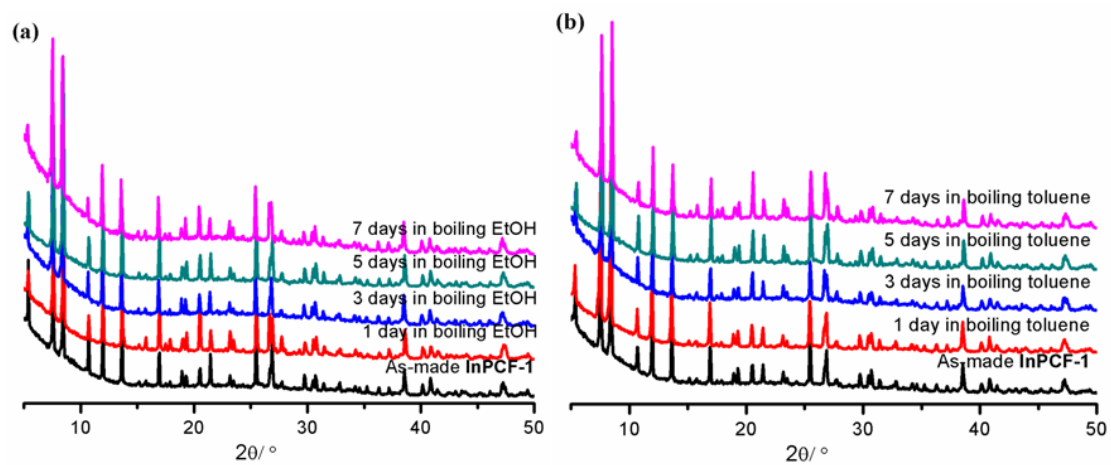


Figure S4 The PXRD patterns for InPCF-1 measured during chemical stability tests. (a) In refluxing EtOH at 80 °C for up to 7 days. (b) In refluxing toluene at 110 °C for up to 7 days.

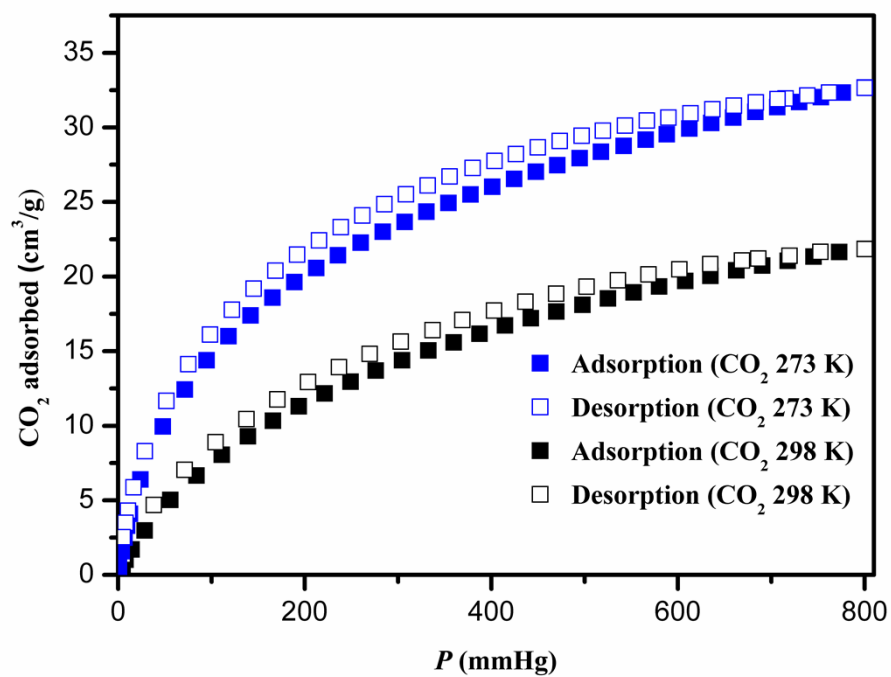


Figure S5 The CO₂ isotherms at 273 K and 298 K for InPCF-1.

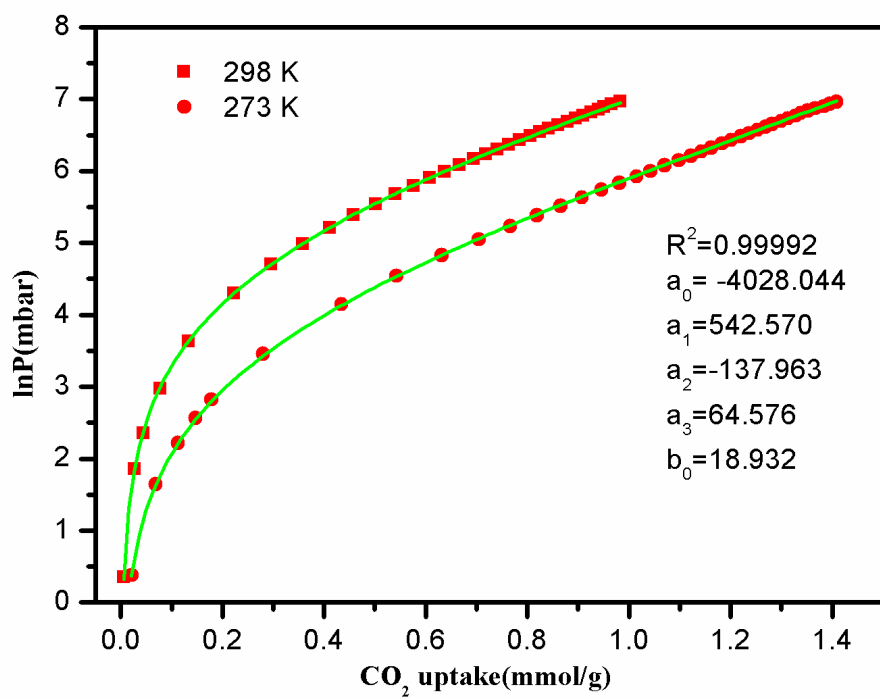


Figure S6 The CO₂ isotherms at 273 K and 298 K (symbols) and the Virial equation fits (lines) for InPCF-1.

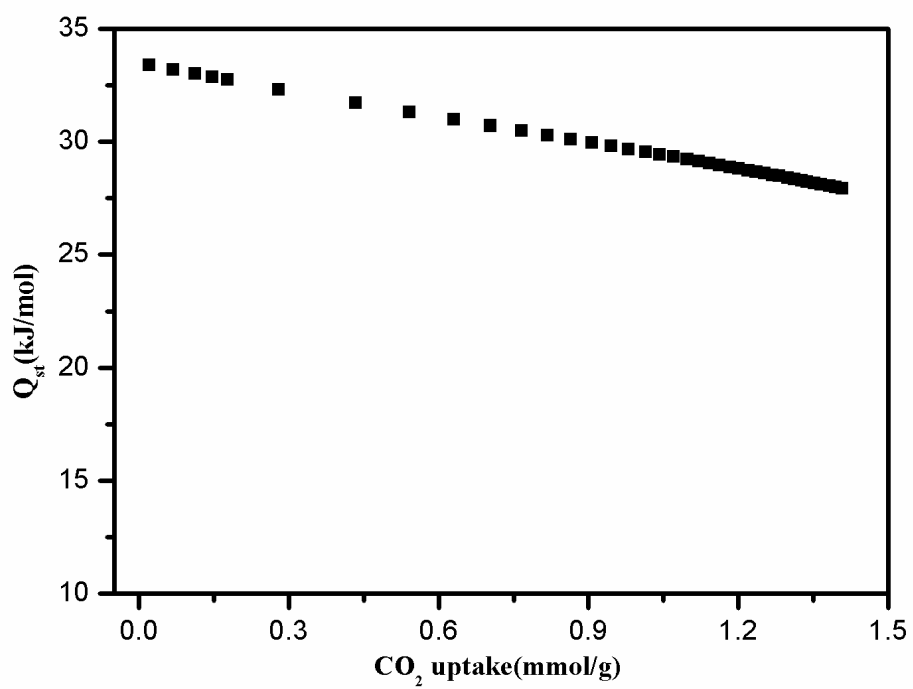


Figure S7 Isosteric heats of CO_2 adsorption for **InPCF-1**

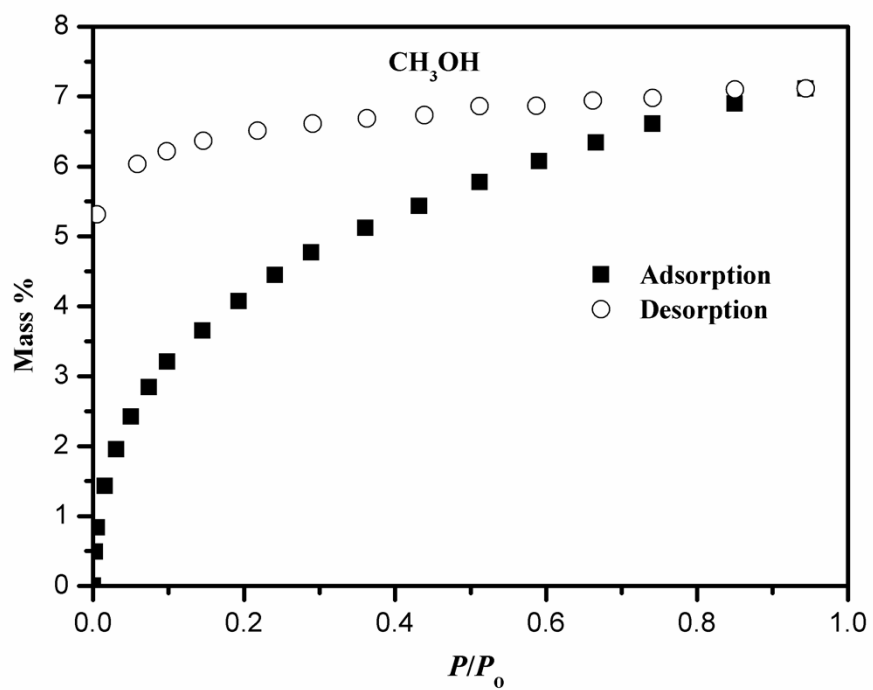


Figure S8 The CH₃OH isotherm at 298 K for InPCF-1.

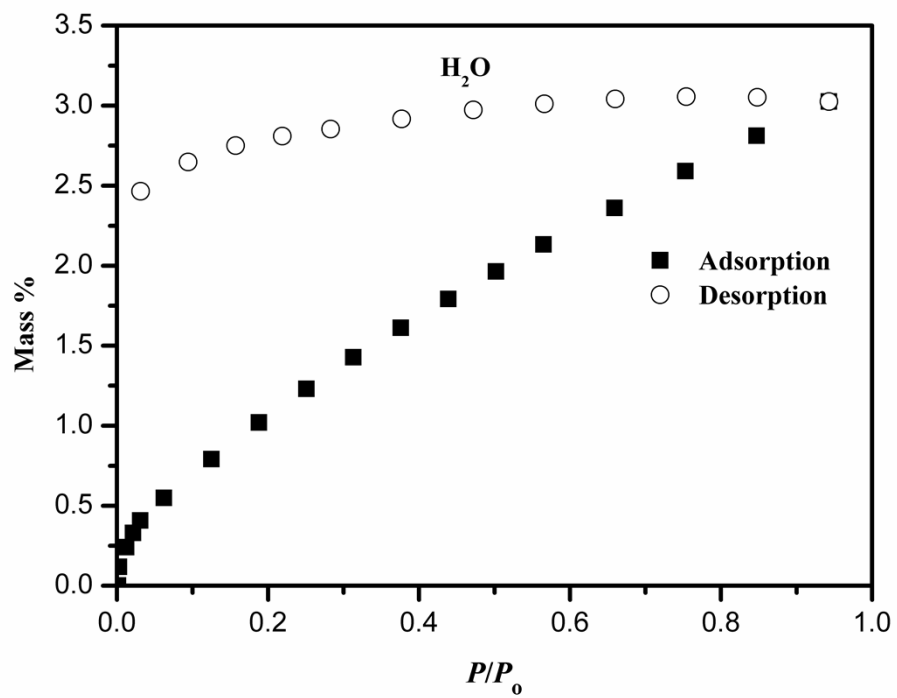


Figure S9 The H₂O isotherm at 298 K for InPCF-1.

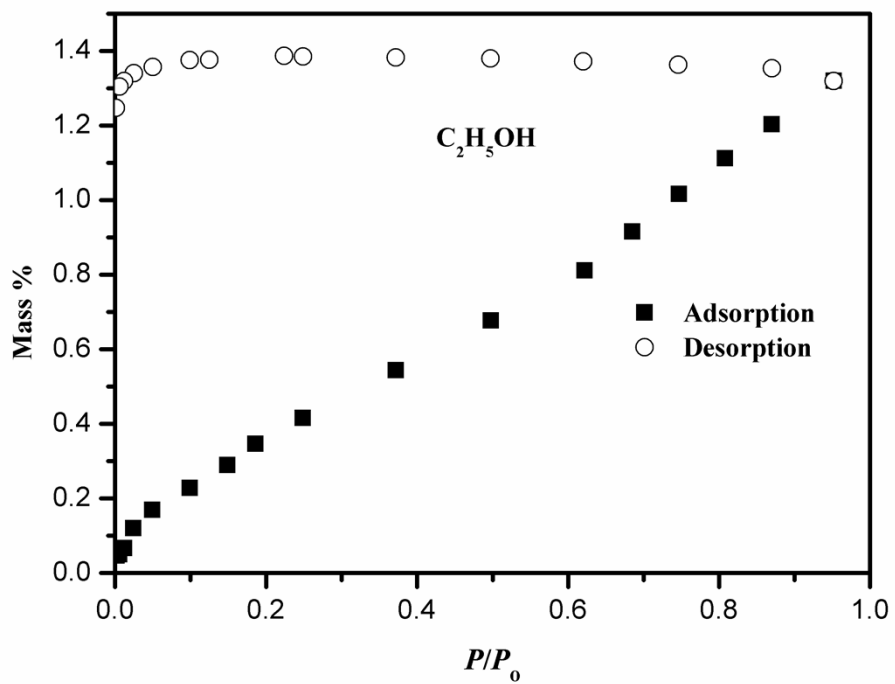


Figure S10 The C_2H_5OH isotherm at 298 K for InPCF-1.

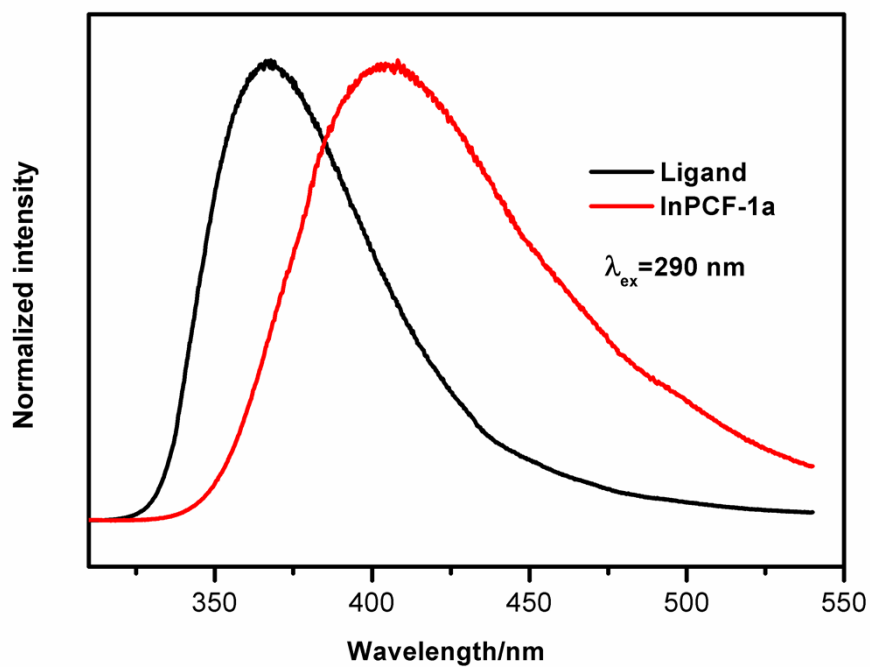


Figure S11 Solid state luminescence spectra of ligand and **InPCF-1a** upon excitation at 290 nm at room temperature.

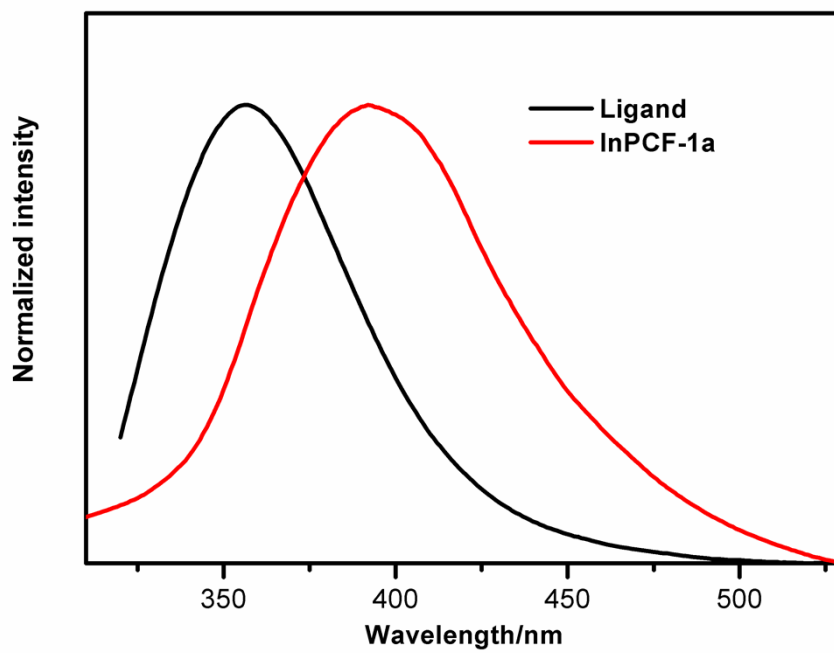


Figure S12 Luminescence spectra of ligand and **InPCF-1a** in DMF solution upon excitation at 290 nm.

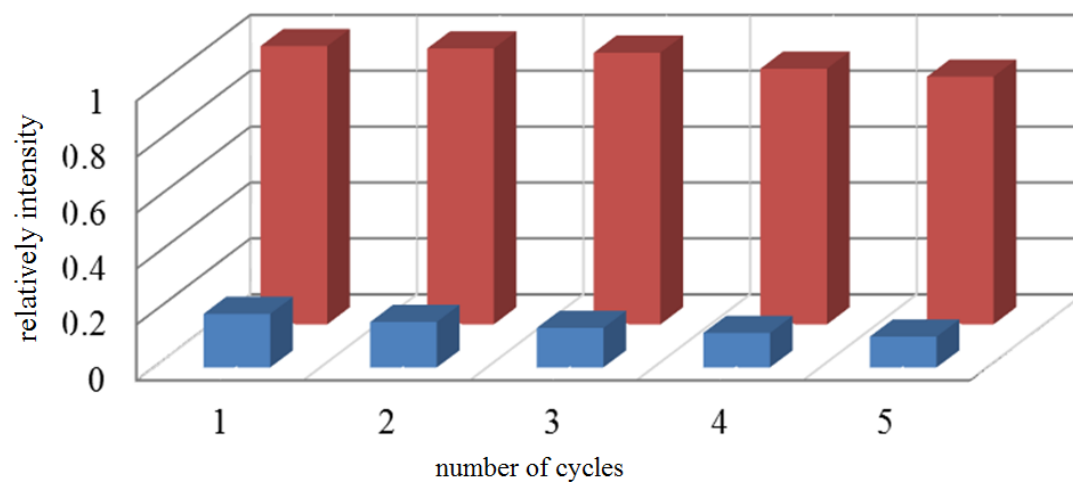


Figure S13 Multiple cycles for the quenching by $\text{Cu}(\text{NO}_3)_2$ and the recovery after filtration and ultrasonic washing by DMF for three times. The red bars show the pristine intensity and regenerated ones after washing; while the blue bars show the intensities after addition of $\text{Cu}(\text{NO}_3)_2$ @DMF solutions

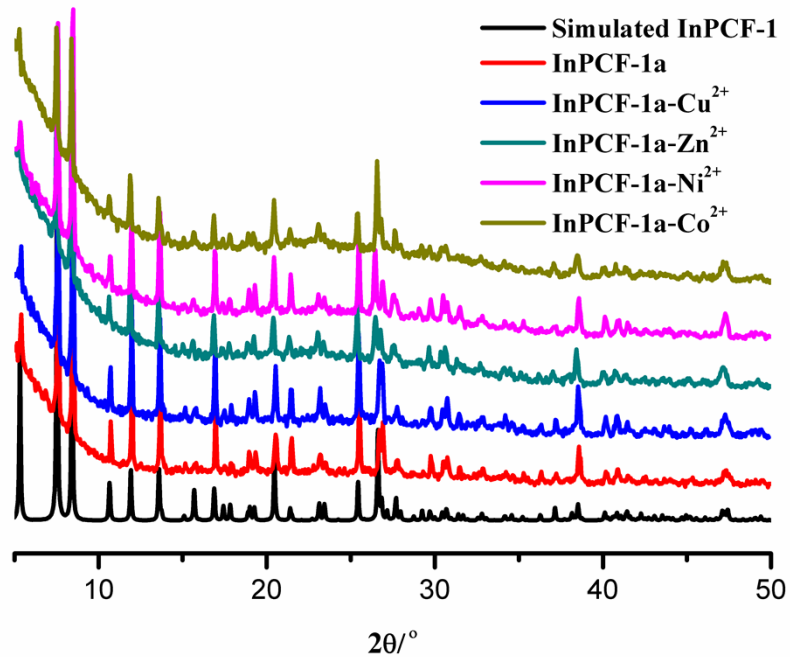


Figure S14 PXRD of **InPCF-1a** and sample after immersing $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Cu}^{2+}$ Zn^{2+} Ni^{2+} Co^{2+}) DMF solution

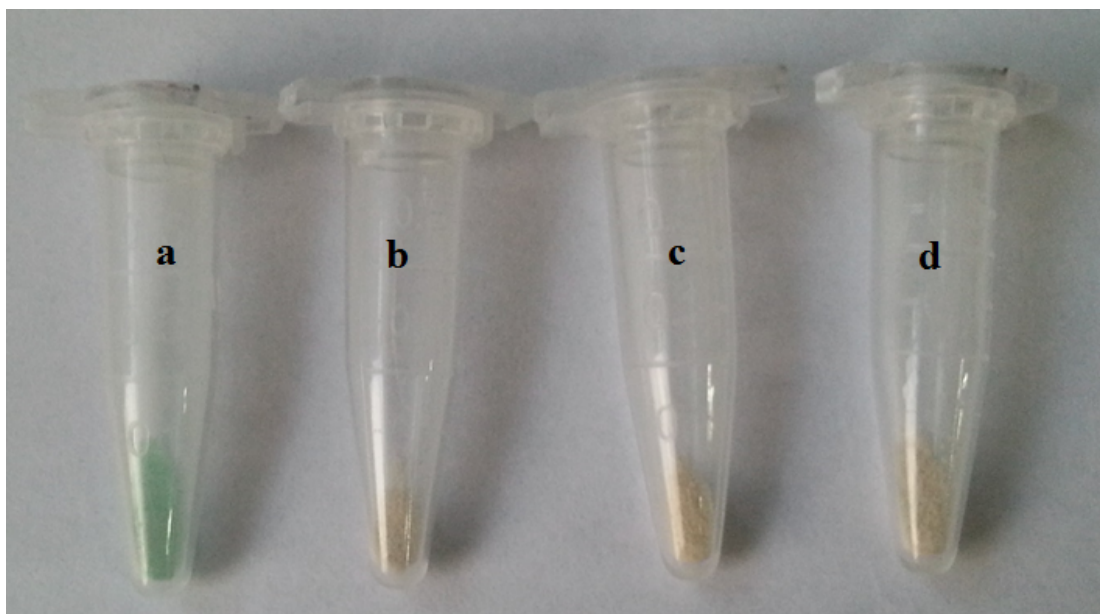


Figure S15 Photographs of **InPCF-1a** soaked in DMF solution containing $M(\text{NO}_3)_2$ with 10^{-2} M, a) Cu^{2+} , b) Co^{2+} , c) Ni^{2+} , d) Zn^{2+} for 24 h.

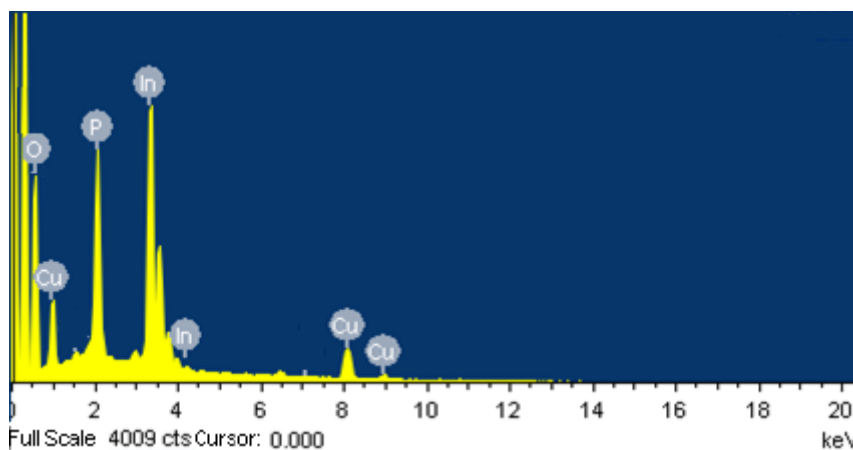


Figure S16 The EDS of the solid samples of **InPCF-1a-Cu²⁺** obtained by centrifugal separation of **InPCF-1a** soaked in DMF solution containing $M(NO_3)_2$ with 10^{-2} M, washing with DMF , and drying in 60 °C oven.

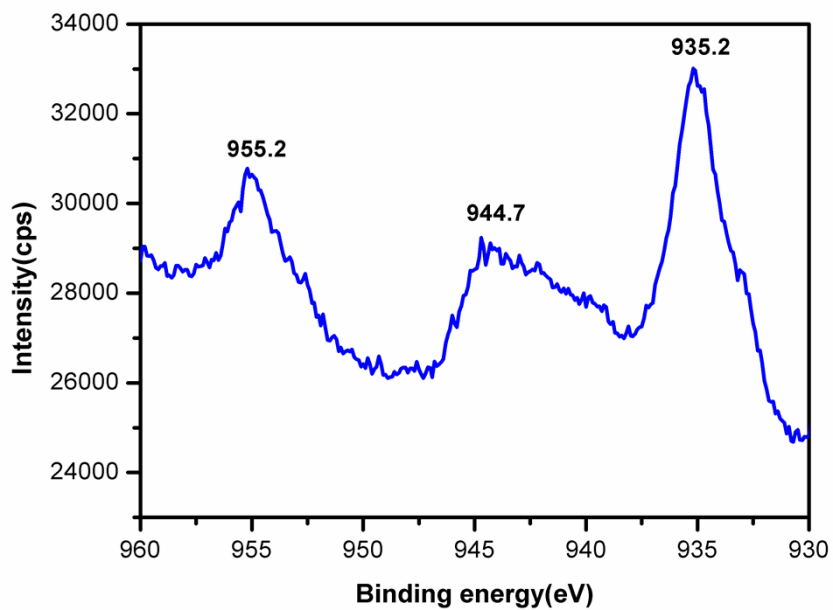


Figure S17 X-ray photoelectron spectroscopy (XPS) spectra of Cu²⁺-incorporated **InPCF-1a**.

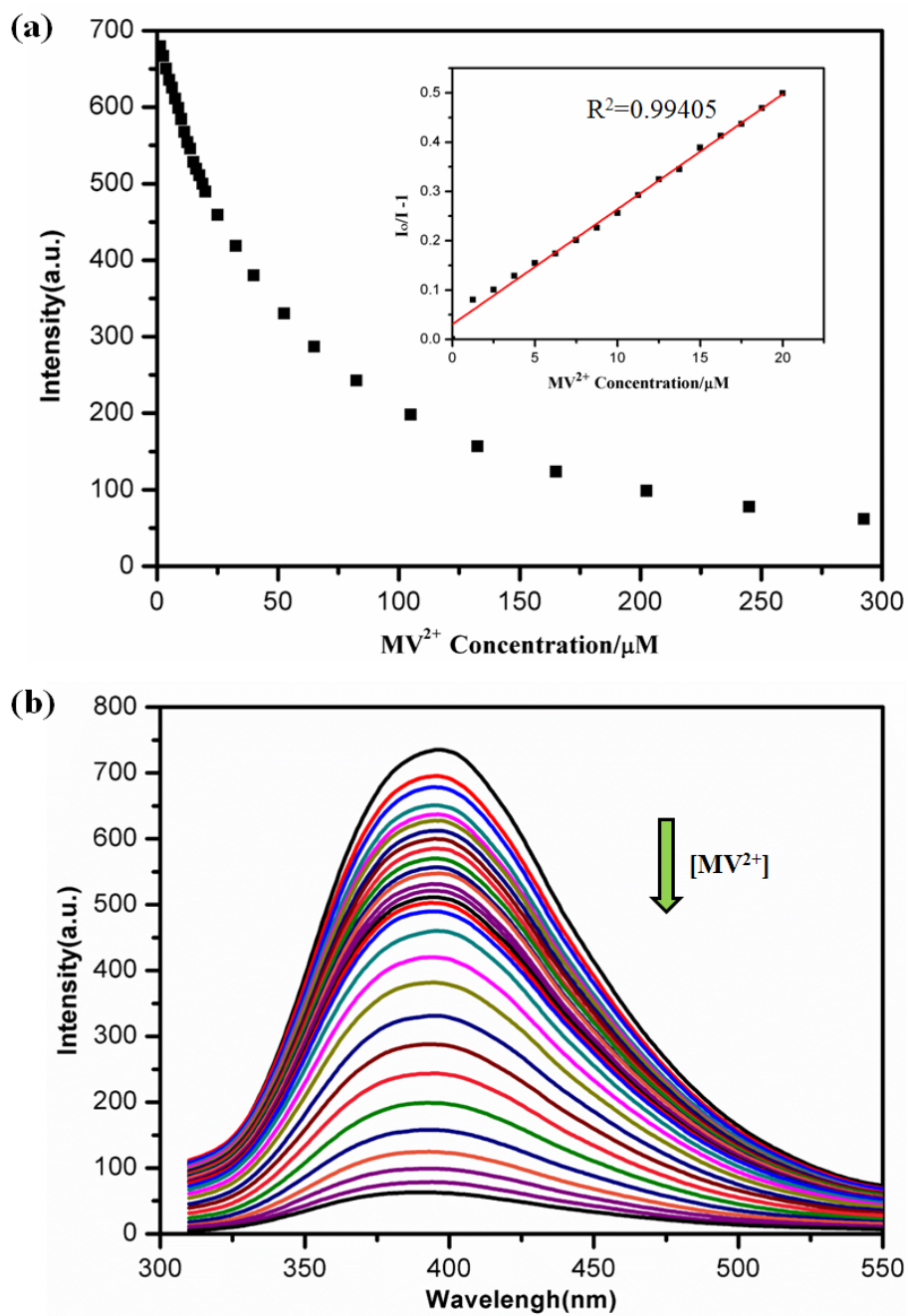


Figure S18 (a) and (b) Concentration-dependent luminescence intensities of **InPCF-1a** by the addition of different contents of MV^{2+} DMF solution (Ex at 290 nm)

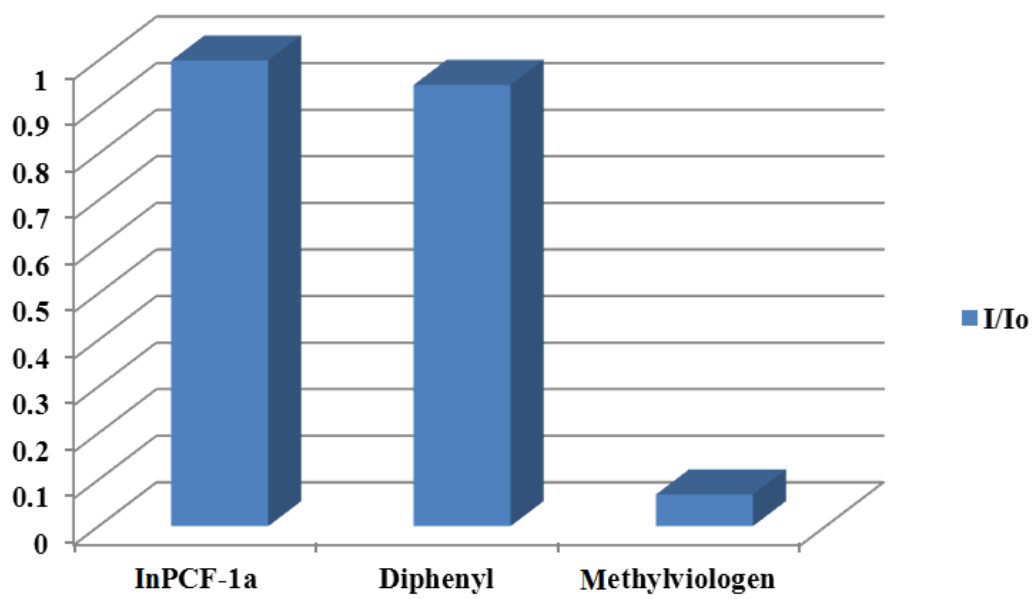


Figure S19 Luminescence spectra of **InPCF-1a**, **InPCF-1a** with 29 mM diphenyl, and **InPCF-1a** with 29 mM methylviologen.