Electronic Supplementary Material (ESI) for RSC Advances.

Highly sensitive and selective fluorescent probe for Fe^{3+} and phenol hazardous compounds based on a water-stable Zn-Based metal-organic framework in aqueous media

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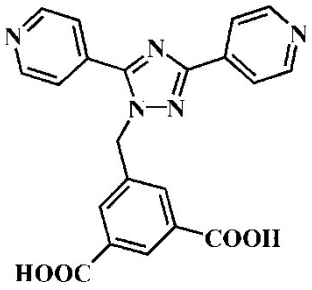


Scheme S1. The ligand used in this article.

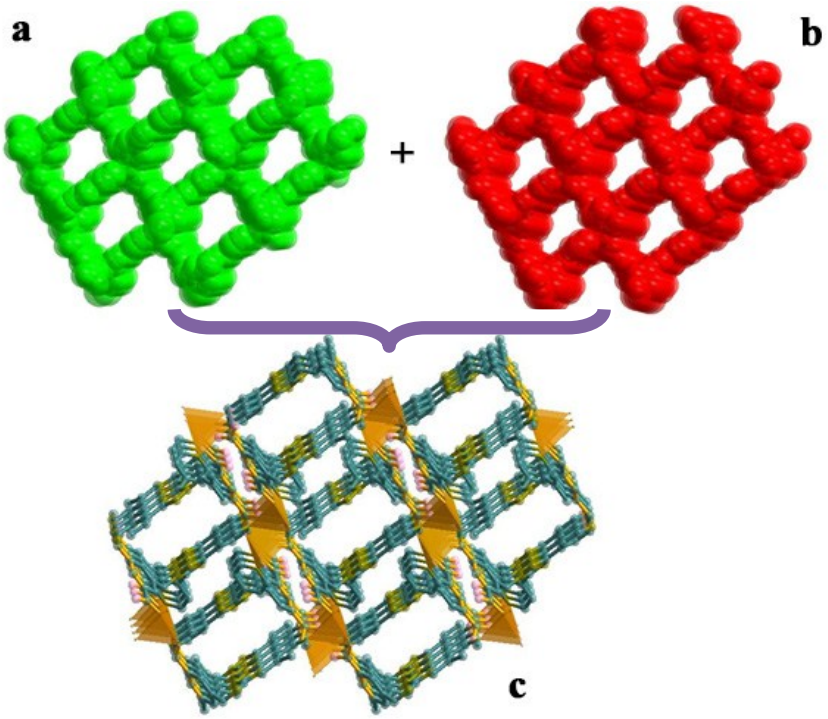


Figure S1. The two-fold interpenetrating network (c) constructed by mutual interpenetration of two three-dimensional frameworks (a and b).

Table S1 Crystal data and structure refinement details of complex **1**[a].

Complex	**HPU-1**
Formula	$C_{22.50}H_{20.5}N_{5.5}O_{6.5}Zn$
formula weight, fw	537.31
Temperature, *T* [K]	293(2)
crystal system	*monoclinic*
space group	*P 21/n*
a [Å]	12.208(3)
b [Å]	13.002(3)
c [Å]	16.101(4)
α [°]	90
β [°]	104.197(4)
γ [°]	90
V [Å^3]	2477.8(10)
Z	4
ρ [g cm^{-3}]	1.440
μ [mm^{-1}]	1.041
θ range	2.45-20.78
F(000)	1104.0
goodness-of-fit, GOF	1.008
R_1[a] [I > 2σ (I)]	0.0425
wR_2[b] (all data)	0.1129

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|^2]^{1/2}$.

Table S2 Selected Bond Distances (A°) and Angles (°) for Compound **1**

1			
Zn(1)-O(4)	1.9213(18)	Zn(1)-O(1)#1	1.9708(19)
Zn(1)-N(5)#2	2.0269(19)	Zn(1)-N(1)#3	2.056(2)
O(4)-Zn(1)-O(1)#1	113.31(8)	O(4)-Zn(1)-N(5)#2	122.54(8)
O(1)#1-Zn(1)-N(5)#2	105.56(8)	O(4)-Zn(1)-N(1)#3	112.72(8)
O(1)#1-Zn(1)-N(1)#3	95.28(8)	N(5)#2-Zn(1)-N(1)#3	103.64(8)

Symmetry transformations used to generate equivalent atoms for **1**: #1 x+1/2, -y-1/2, z+1/2; #2 x-1/2, -y-1/2, z+1/2; #3 x, y-1, z.

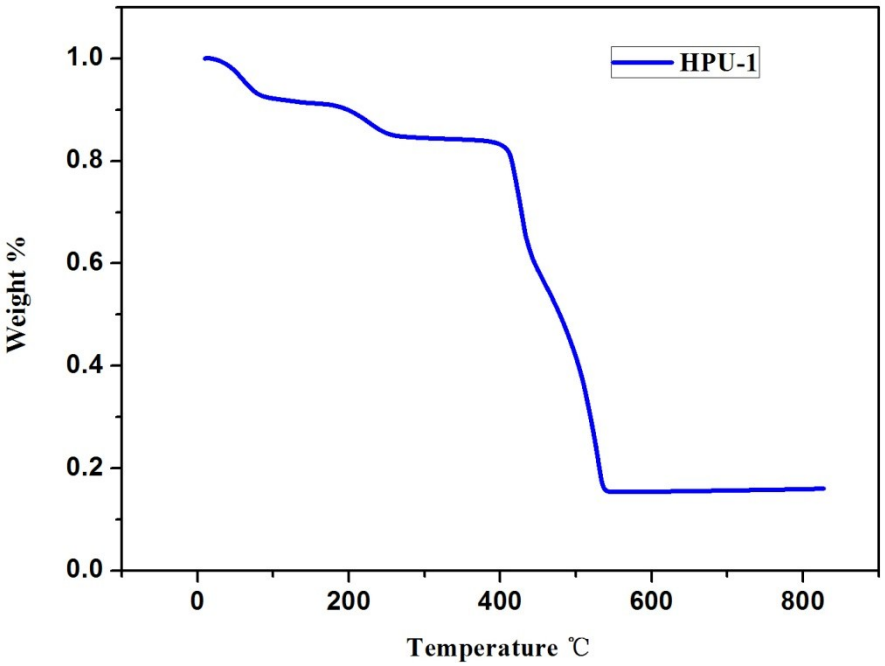


Figure S2. The TG curve of **HPU-1**.

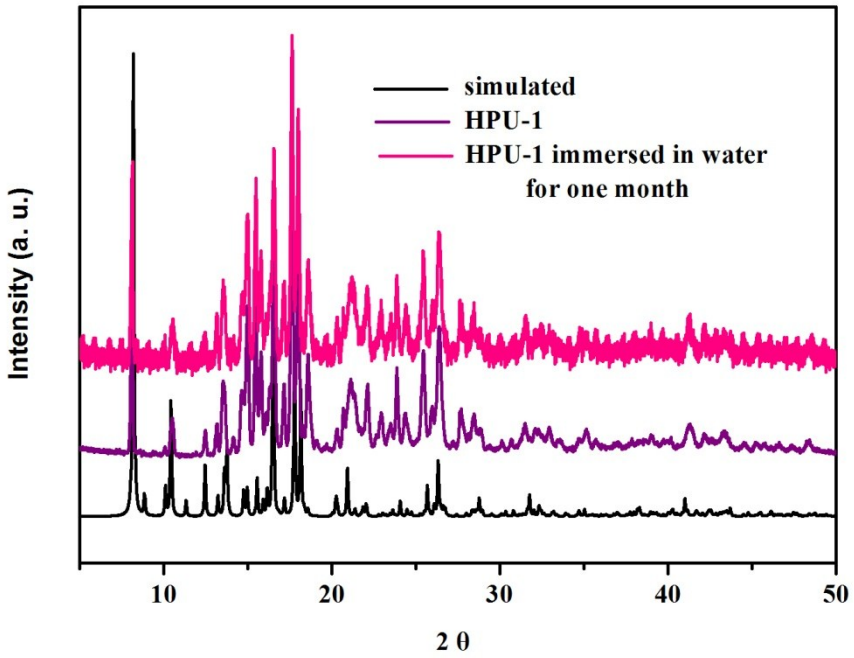


Figure S3. PXRD patterns of the simulated, as-synthesized of **HPU-1** and immersed in water for one month.

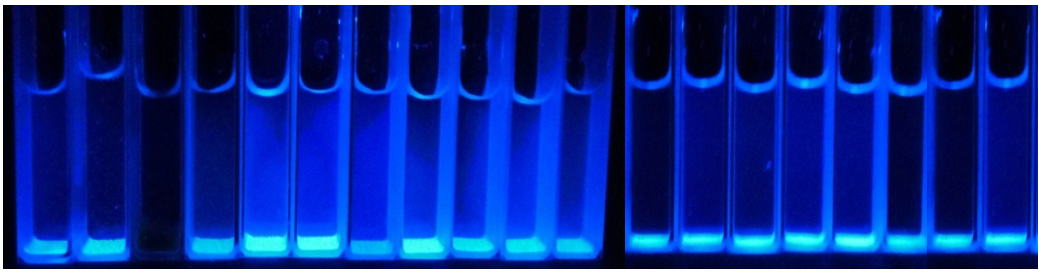


Figure S4. The corresponding photographs for **HPU-1** in the presence of various 0.01 mol/L aqueous of M^{n+} under UV-light irradiation at 350 nm. From the left to right: **HPU-1**, Cr^{3+}, Fe^{3+}, Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Eu^{3+}, Tb^{3+}.

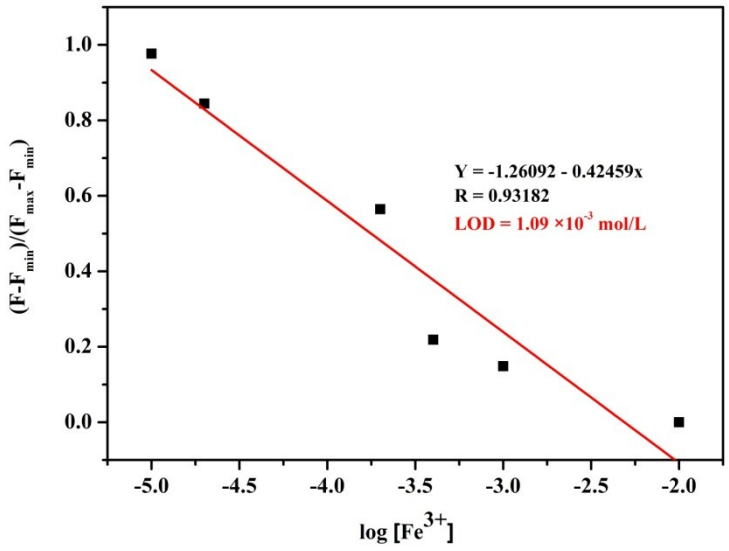


Figure S5. The normalized response of fluorescence calibration value at 430 nm as a function of Fe^{3+} concentration.

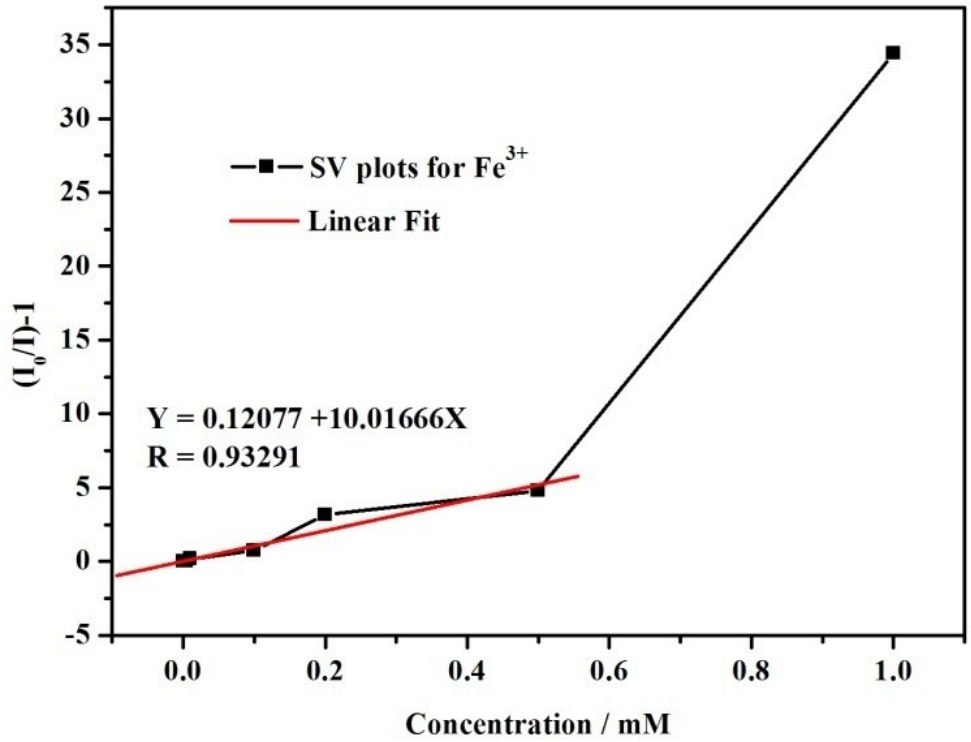


Figure S6. The fluorescence intensities at 430 nm as a function of Fe^{3+} concentration.

Table S3 The comparison of coefficients of quenching

Ksv values (M^{-1})	Complexes
4.1×10^3	EuL_3 (L = 4′-(4-carboxyphenyl)-2,2′: 6′,2″-terpyridine)[1]
7.8×10^3	Pb_3O_2L (H_2L =4-(1H-tetrazol-5-yl)phenol)[2]
3.543×10^3	$\{[Tb_4(OH)_4(DSOA)_2(H2O)8]\cdot(H_2O)_8\}_n$[3]
2.09×10^4	Eu−HODA (HODA = 2,2′,3,3′-Oxidiphthalic acid)[4]
1.0×10^4	This work

1 Zheng, M.; Tan, H.-Q.; Xie, Z.-G.; Zhang, L.-G.; Jing, X.-B. and Sun, Z.-C. *ACS Appl. Mater. Interfaces*., **2013**, *5*, 1078−1083.

2 Luo, X.; Zhang, X.; Duan, Y.-L.; Wang, X.-L.; Zhao, J.-M. *Dalton Trans.*, **2017**, *46*, 6303-6311.

3 Dong, X.-Y.; Wang, R.; Wang, J.-Z.; Zang, S.-Q.; Mark, T. C. W. *J. Mater. Chem. A.*, **2015**, *3*, 641-647.

4 Wang, J.; Jiang, M.; Yan, L.; Peng, R.; Huangfu, M. J.; Guo, X.-X.; Li, Y.; Wu, P.-Y. *Inorg. Chem*., **2016**, *55*, 12660−12668.

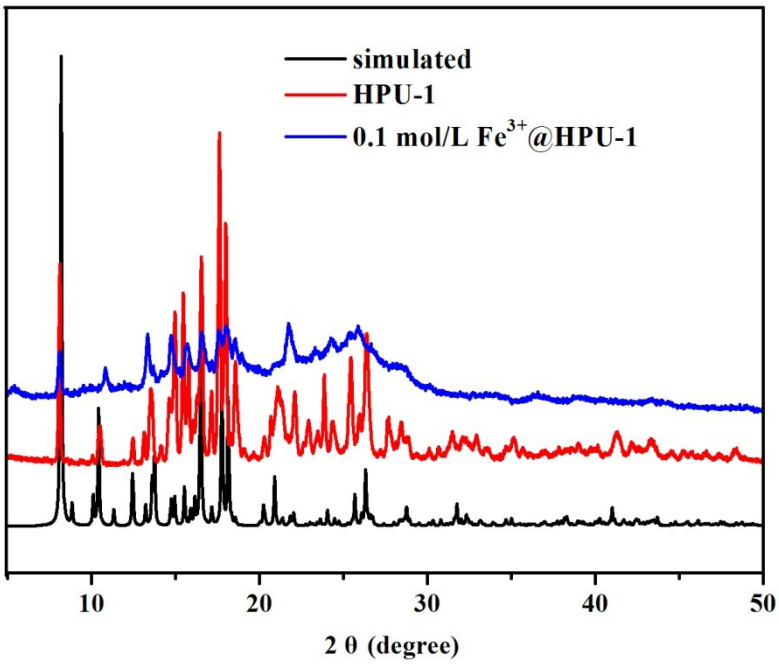


Figure S7. PXRD patterns of simulated **HPU-1**, experimental **HPU-1** and 0.1 mol/L Fe^{3+}@ **HPU-1**.

Table S4 The ICP results of time-dependent filtrate after ion-exchanging

Immersion time in Fe^{3+} aqueous solution	Zn^{2+} ion amount (ppm) filtrate after Fe^{3+} exchanging observed in ICP results	Fe^{3+} ion amount (ppm) filtrate after Fe^{3+} exchanging observed in ICP results
30 min	241.8	796.4
1 h	330.6	788.1
2 h	426.7	772.4
5 h	510.0	764.2
16 h	638.1	692.5
24 h	740.1	659.0

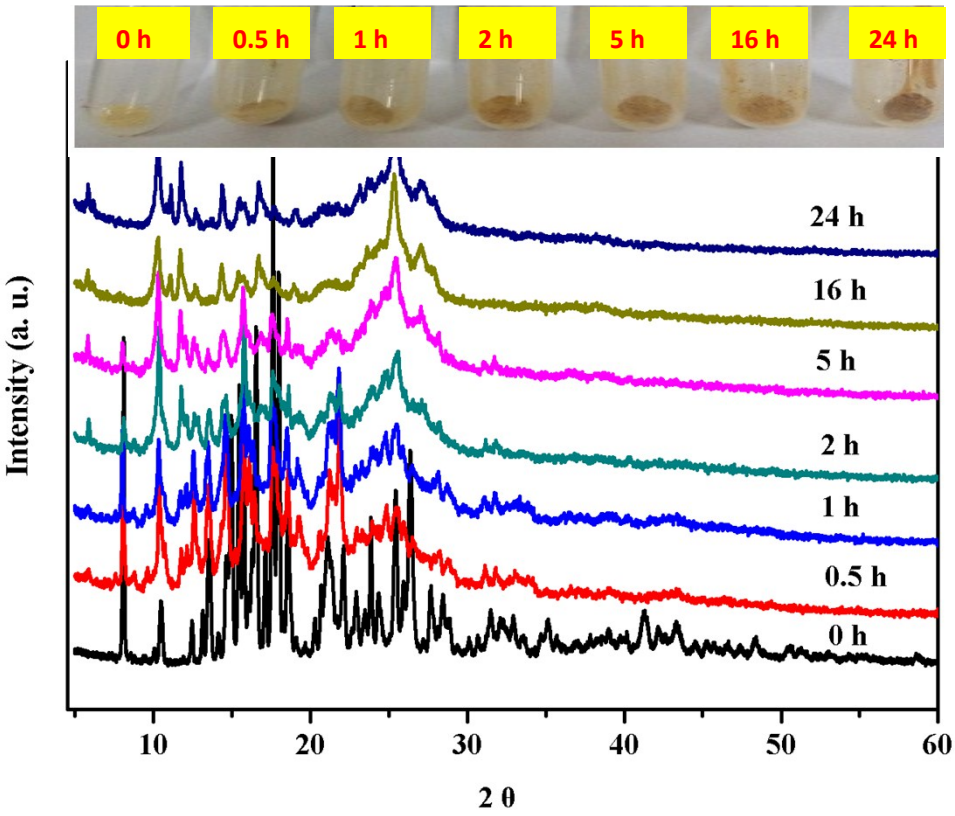
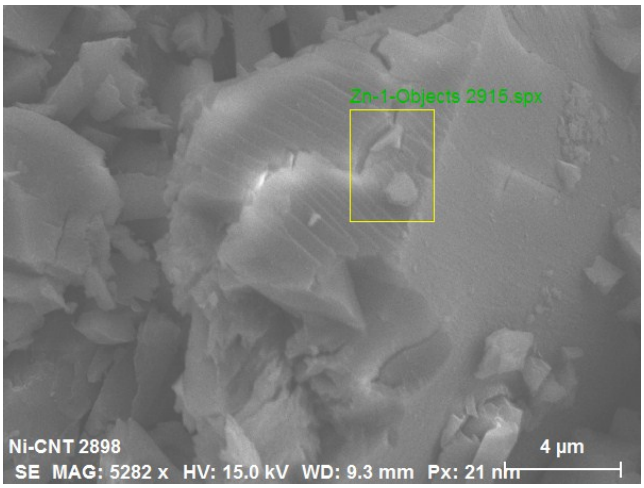
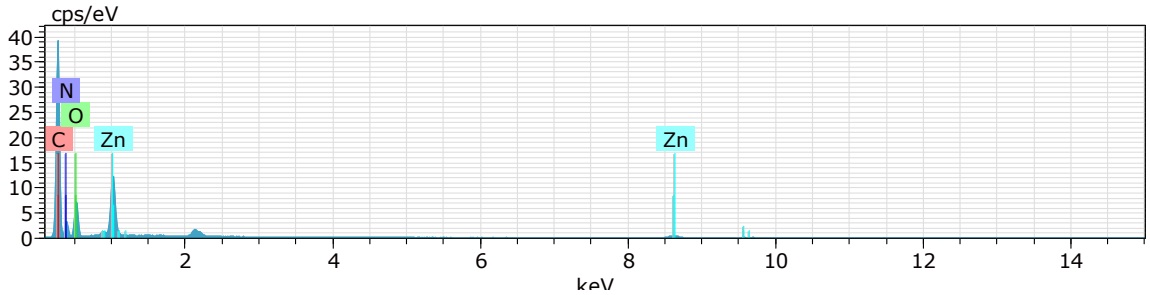


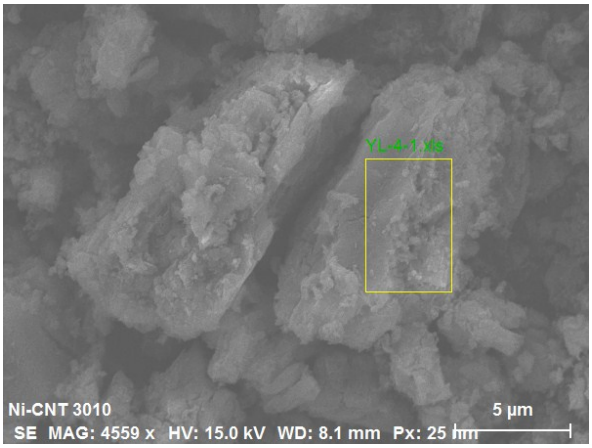
Figure S8. The PXRD patterns of Time-dependent products.

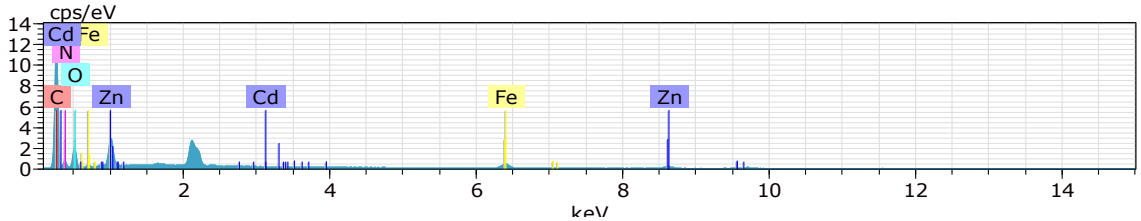




El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	67.38	50.65	60.38	7.71
O	8	K-series	27.35	20.56	18.40	3.59
N	7	K-series	24.71	18.58	18.99	3.63
Zn	30	K-series	13.59	10.22	2.24	0.54

Figure S9. SEM and EDS results of **HPU-1**.





El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	29.34	52.63	67.22	3.50
O	8	K-series	8.39	15.06	14.44	1.22
Zn	30	K-series	7.70	13.81	3.24	0.33
N	7	K-series	6.81	12.22	13.38	1.20
Fe	26	K-series	3.48	6.24	1.71	0.14
Cd	48	L-series	0.00	0.00	0.00	0.00

Figure S10. SEM and EDS results of Fe^{3+}@**HPU-1**.

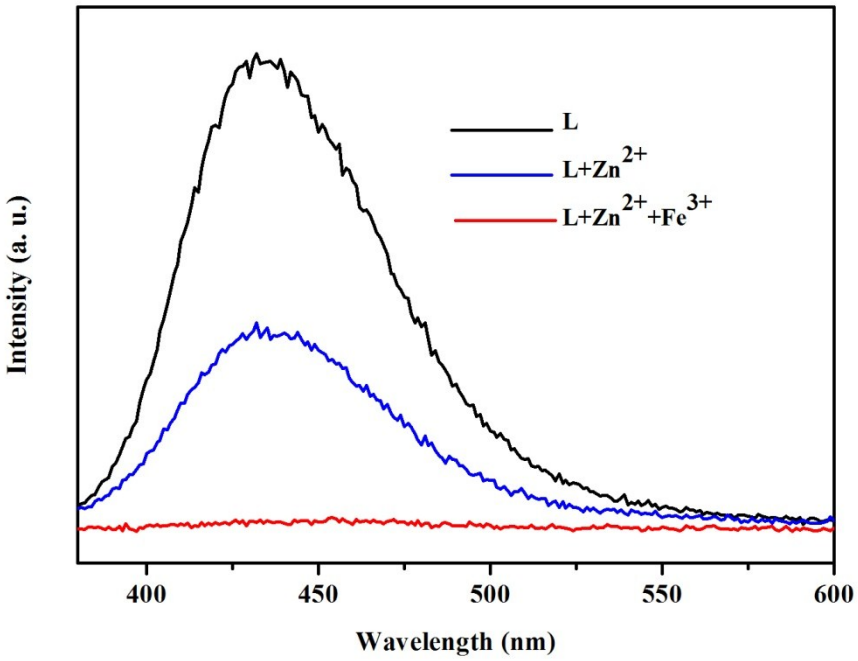


Figure S11. Fluorescence spectra of DPTMIA (2 mg) towards aqueous solution of 0.01 mol/L Zn^{2+}, Zn^{2+} + Fe^{3+} and comparison with free DPTMIA.

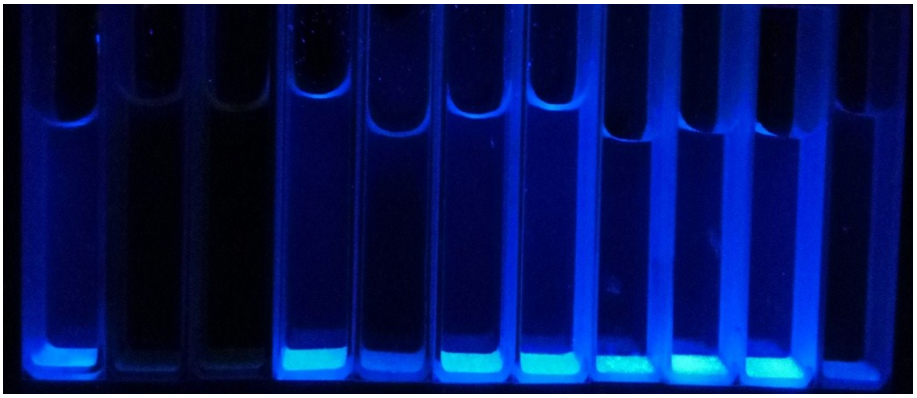


Figure S12. The corresponding photographs for **HPU-1** in the presence of various 0.01 mol/L aqueous of organic analytes under UV-light irradiation at 350 nm. From the left to right: **HPU-1**, 4-NP, 2, 4-DNP, 1, 3-DNB, 3-NP, 2, 4-DNT, 4-NT, 1, 4-DMB, MB, 1, 3, 5-TMB, NB.

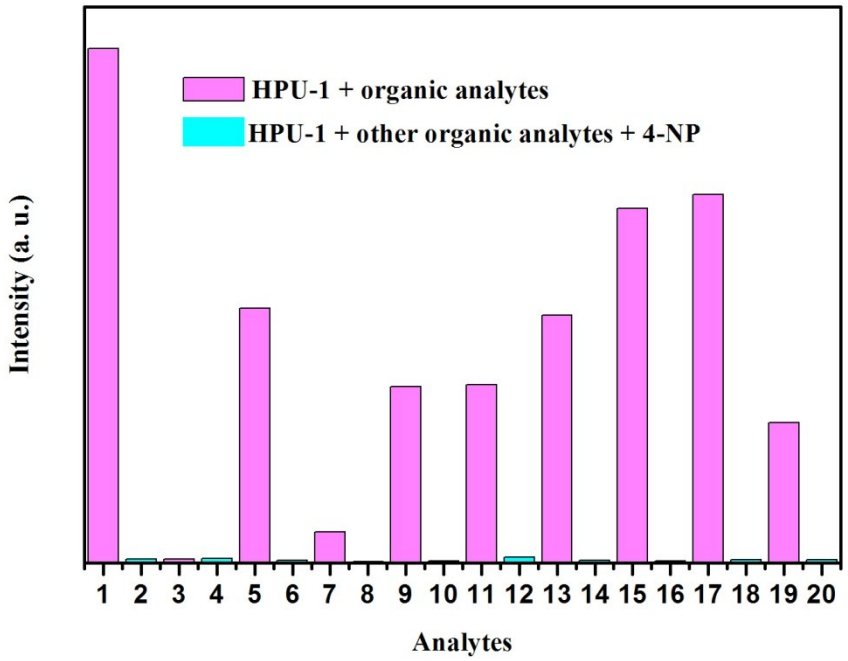


Figure S13. Fluorescence responses of **HPU-1** (2 mg) in the absence and presence of various organic analytes. Pink bars: a free sensor or a sensor treated with the marked organic analytes. Blue bars: a sensor treated with the marked organic analytes followed by equivalent of 4-NP.

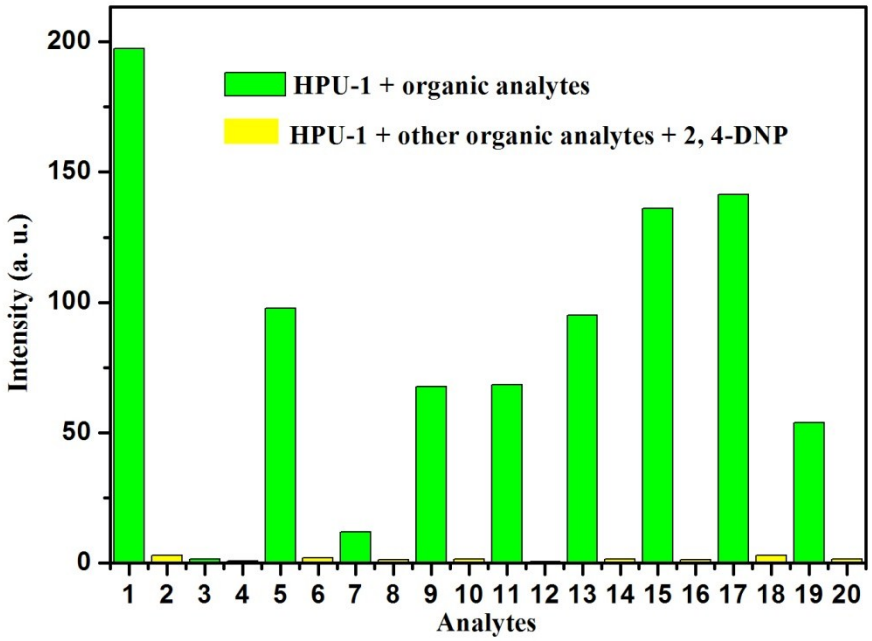


Figure S14. Fluorescence responses of **HPU-1** (2 mg) in the absence and presence of various organic analytes. Cyan bars: a free sensor or a sensor treated with the marked organic analytes. Yellow bars: a sensor treated with the marked organic analytes followed by equivalent of 2, 4-DNP.

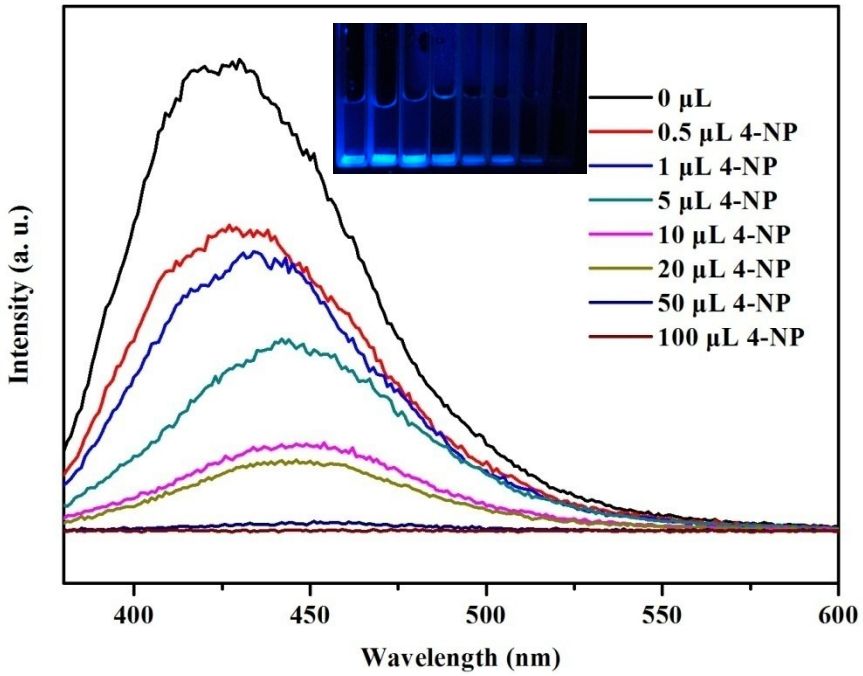


Figure S15. Emission spectra of **HPU-1** (2 mg) dispersed in water (2 mL) upon incremental addition of 4-NP solution (20 mM) in water. Inset: photographs of **HPU-1** (2 mg) in aqueous solutions of various concentrations of 4-NP.

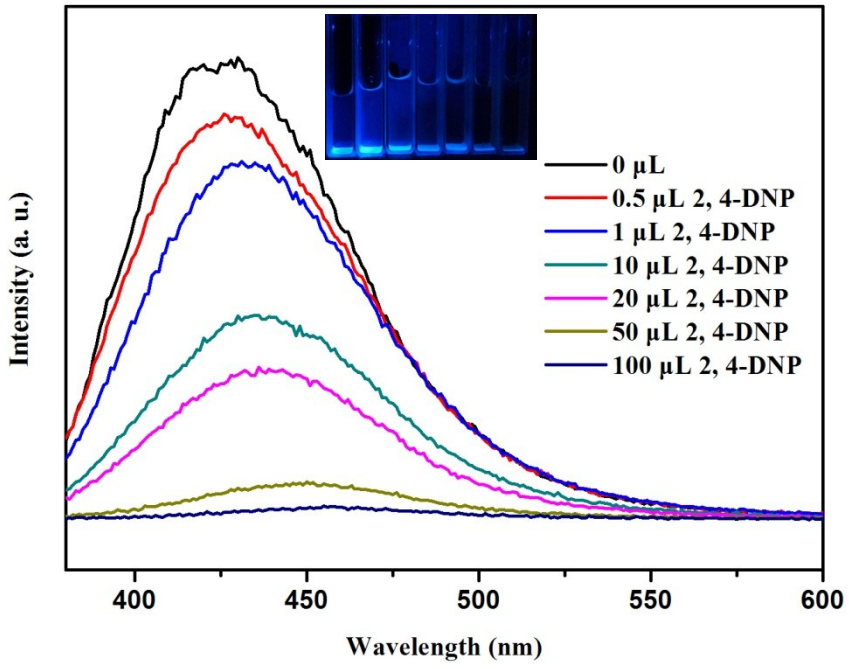


Figure S16. Emission spectra of **HPU-1** (2 mg) dispersed in water (2 mL) upon incremental addition of 2, 4-DNP solution (20 mM) in water. Inset: photographs of **HPU-1** (2 mg) in aqueous solutions of various concentrations of 2, 4-DNP.

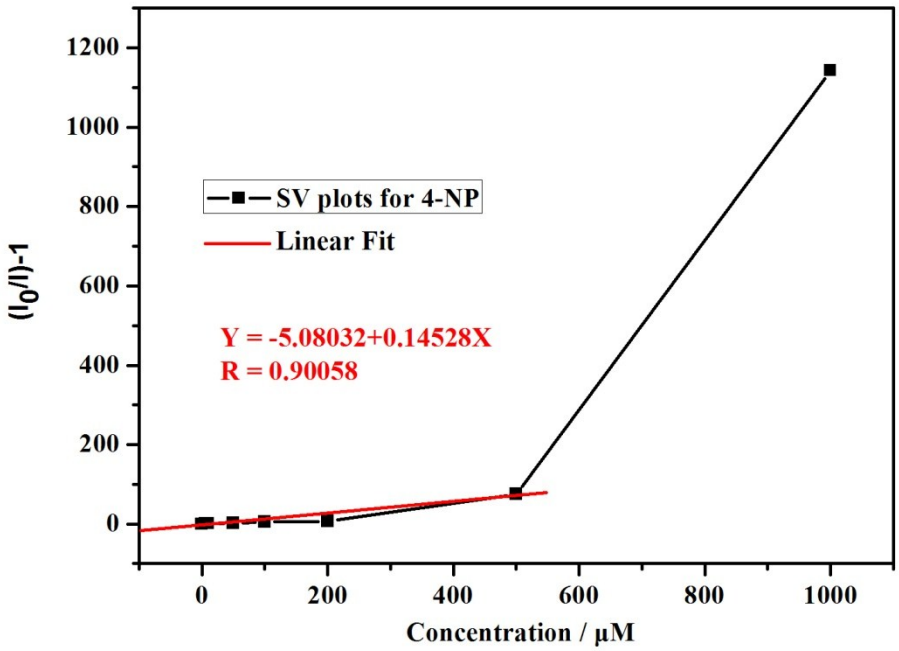


Figure S17. Stern-Volmer (SV) plots for 4-NP. The relative fluorescence intensity is linear with the concentration in the range of 0-500 μM, $I_0/I = 0.14528[Q]-1$. $K_{sv} = 1.45 \times 10^5\ M^{-1}$.

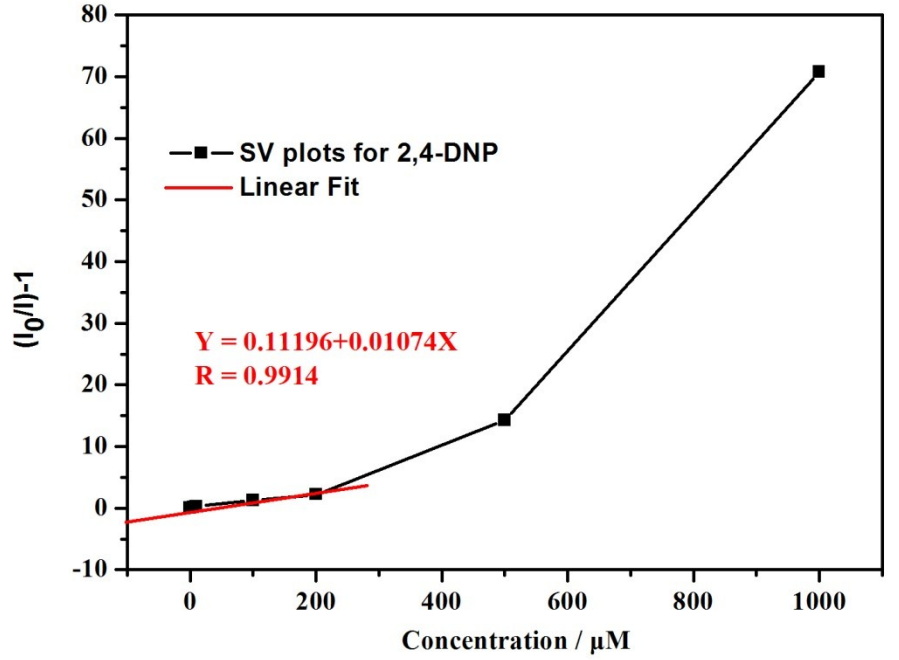


Figure S18. Stern-Volmer (SV) plots for 2, 4-DNP. The relative fluorescence intensity is linear with the concentration in the range of 0-200 μM, $I_0/I = 0.01074[Q]-1$. $Ksv = 1.074 \times 10^4\ M^{-1}$.

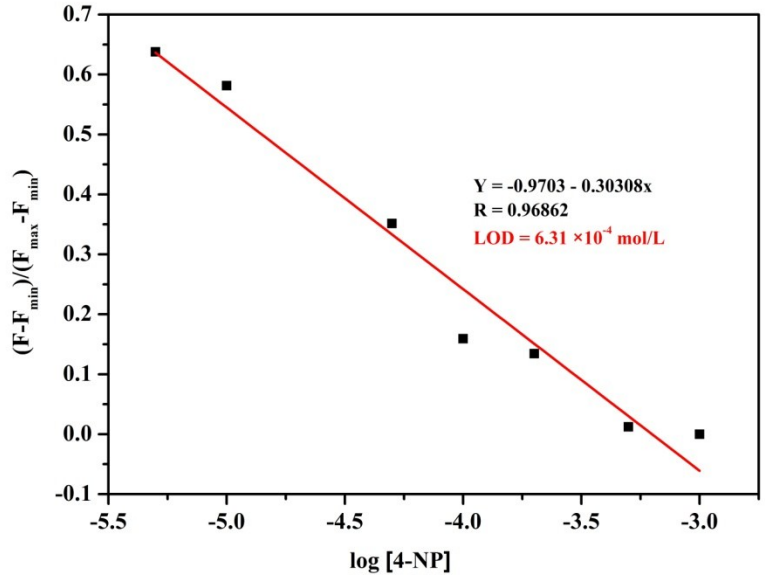


Figure S19. The normalized response of fluorescence calibration value at 430 nm as a function of 4-NP concentration.

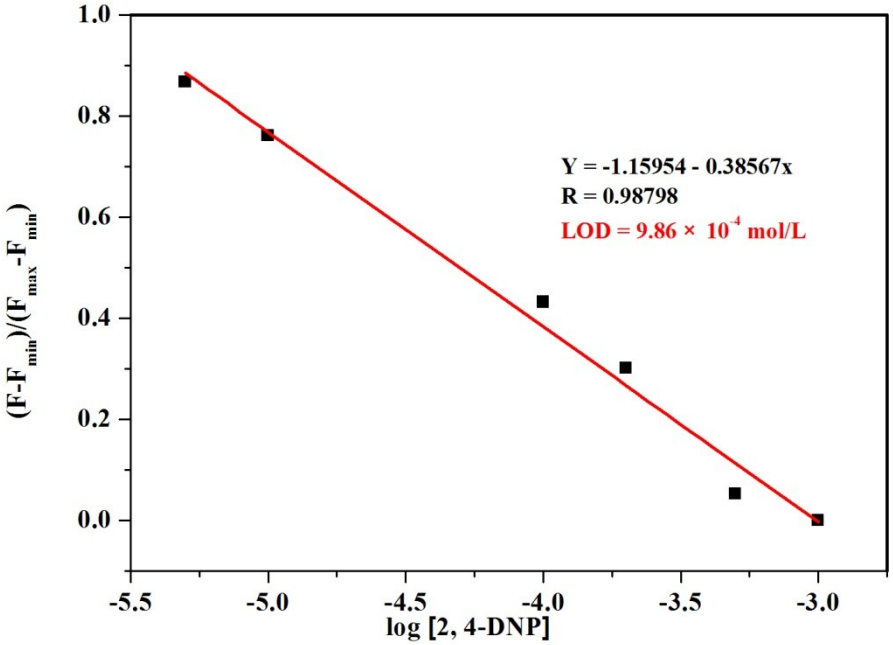


Figure S20. The normalized response of fluorescence calibration value at 430 nm as a function of 2, 4-DNP concentration.

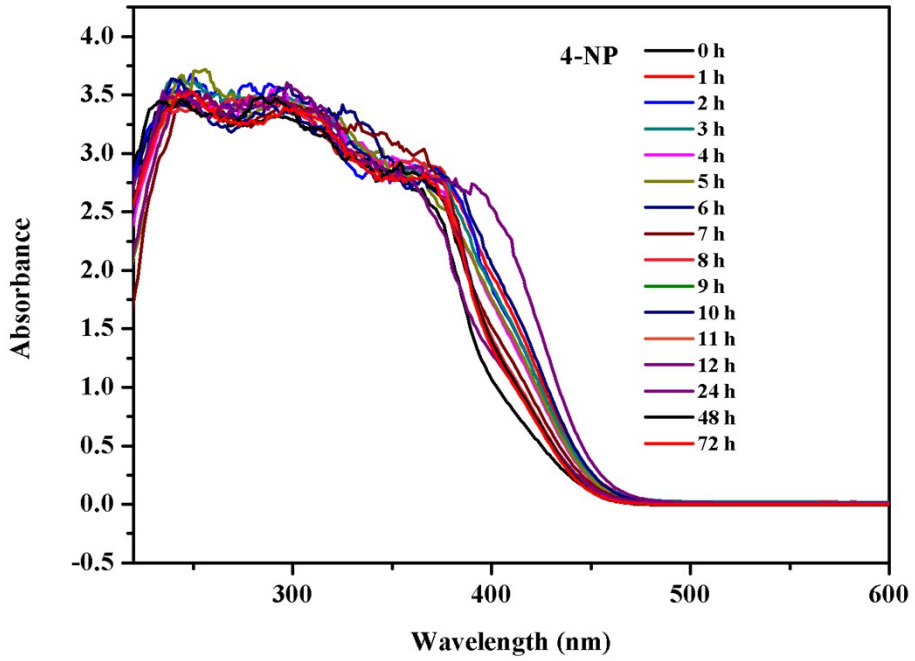


Figure S21. The UV-absorbance spectra of 4-NP in time-dependent filtrate.

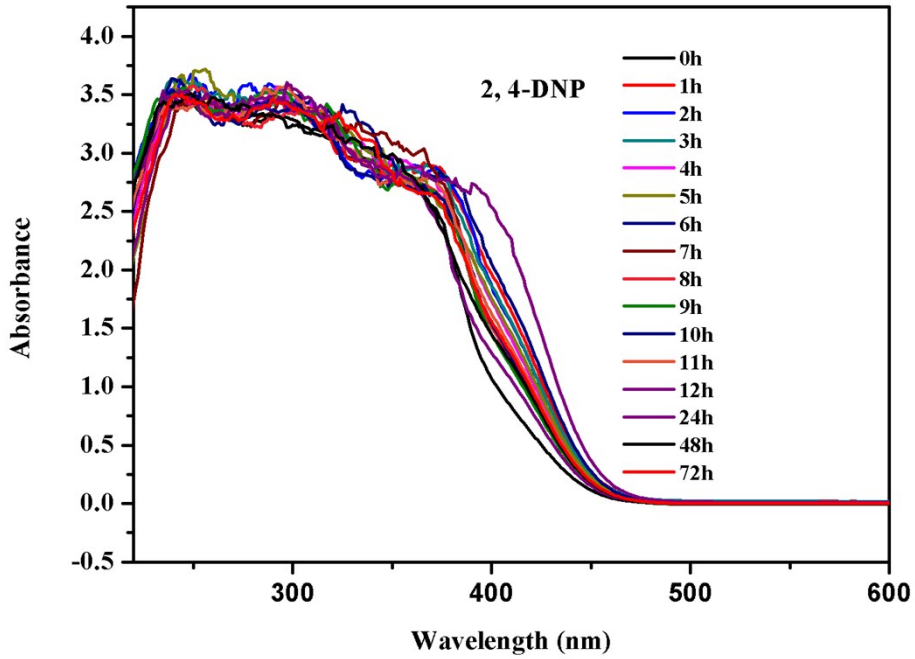


Figure S22. The UV-absorbance spectra of 2, 4-DNP in time-dependent filtrate.

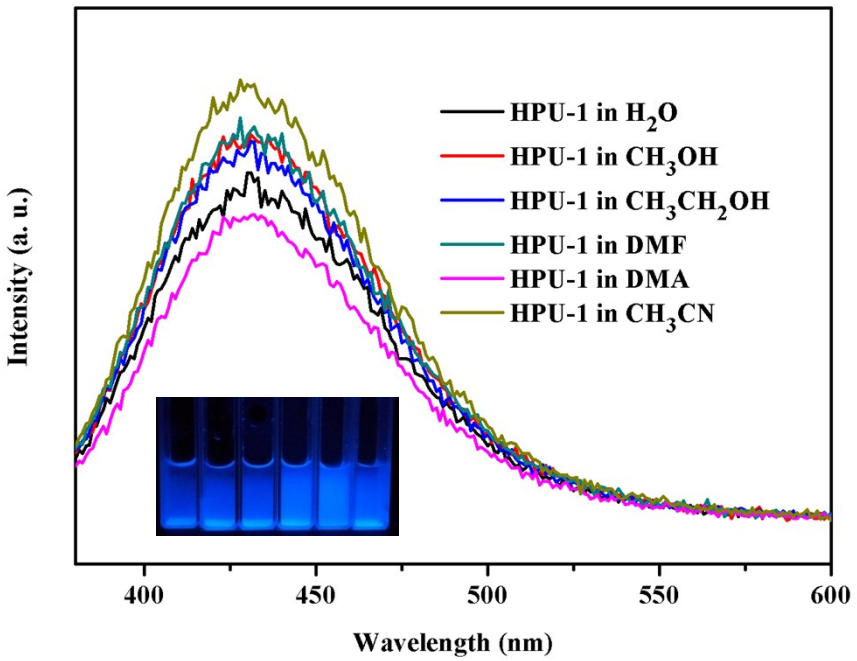


Figure S23. Fluorescence spectra of **HPU-1** (2 mg) in various solvents. **Inset**: photographs of **HPU-1** dispersed in various solvents. From the left to right: H_2O, CH_3OH, CH_3CH_2OH, DMF, DMA, CH_3CN.

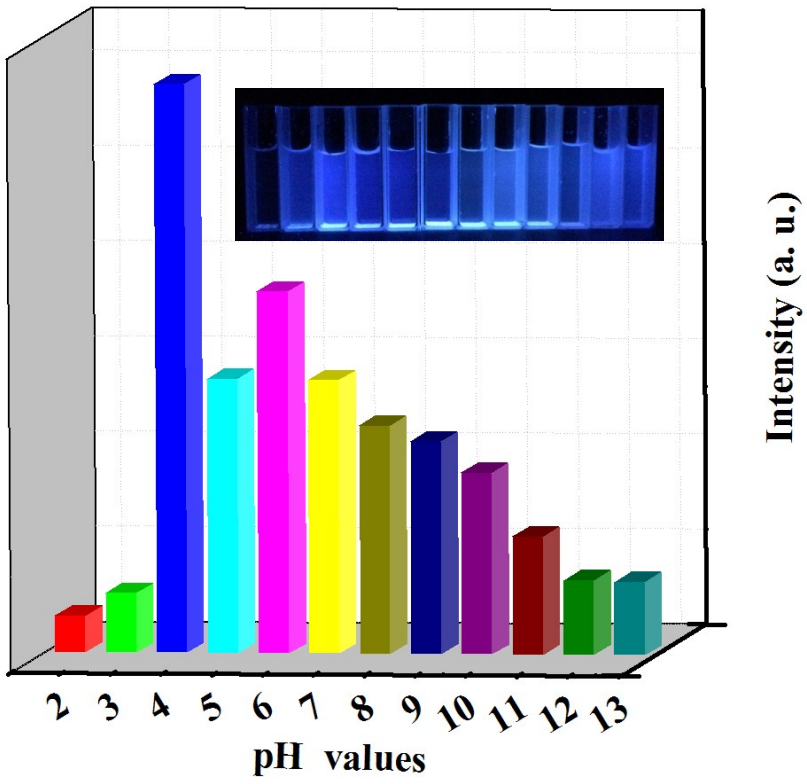


Figure S24. Fluorescence spectra of **HPU-1** (2 mg) in different pH values of aqueous solution (2 mL). **Inset**: photographs of **HPU-1** dispersed in different pH values of aqueous solution.