Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Direct Synthesis of Functionalized PCN-333 via Linker Design for Fe^{3+} Detection in Aqueous Media

Yingmu Zhang, Xinyu Yang, Hong-Cai Zhou*

Department of Chemistry, Texas A&M University, College Station, Texas 77840-3012, USA

Correspondence Author: Dr. Hong-Cai Zhou

Email: zhou@chem.tamu.edu

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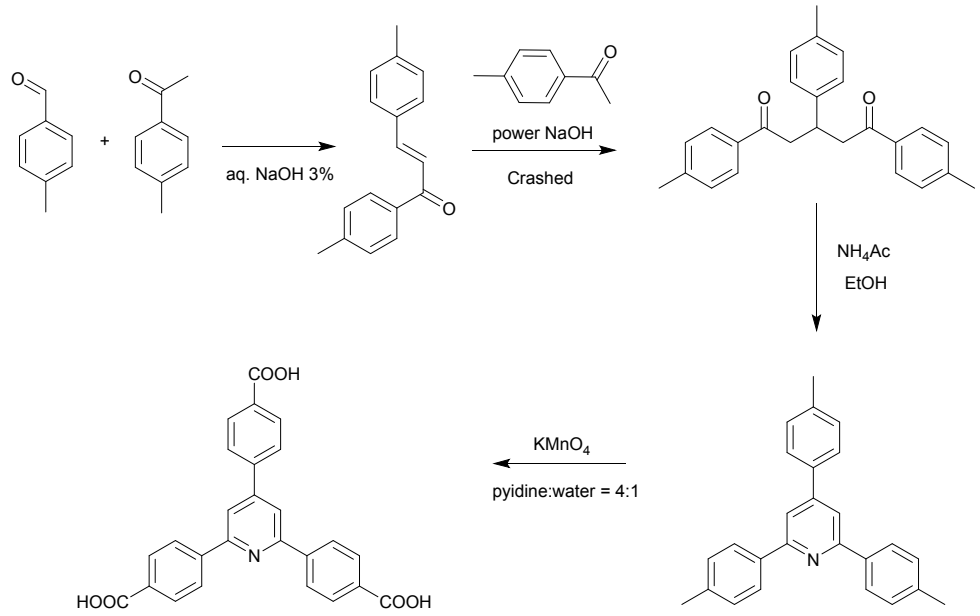
1. Synthesis of ligand H_3PTB



Scheme S1. Synthetic procedures of H_3PTB.

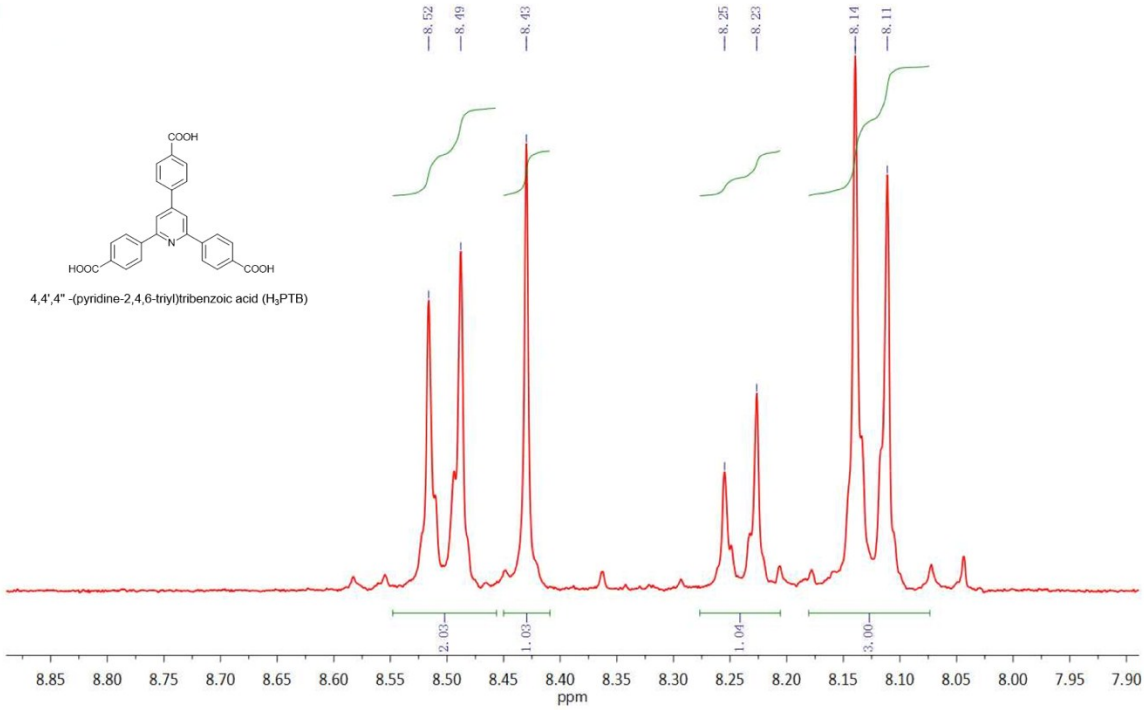


Fig S1. H^1-NMR spectrum of H_3PTB.

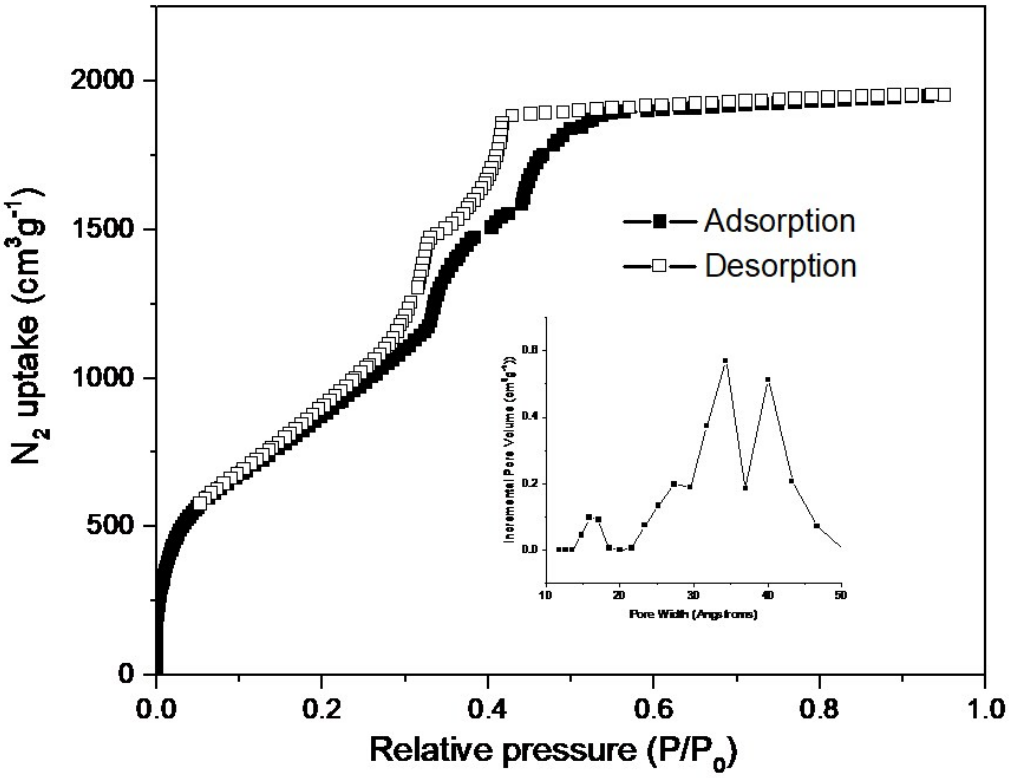


Fig. S2. N_2 sorption isotherm of pristine PCN-604 at 77k, 1 atm. Insert shows the DFT pore size distribution.

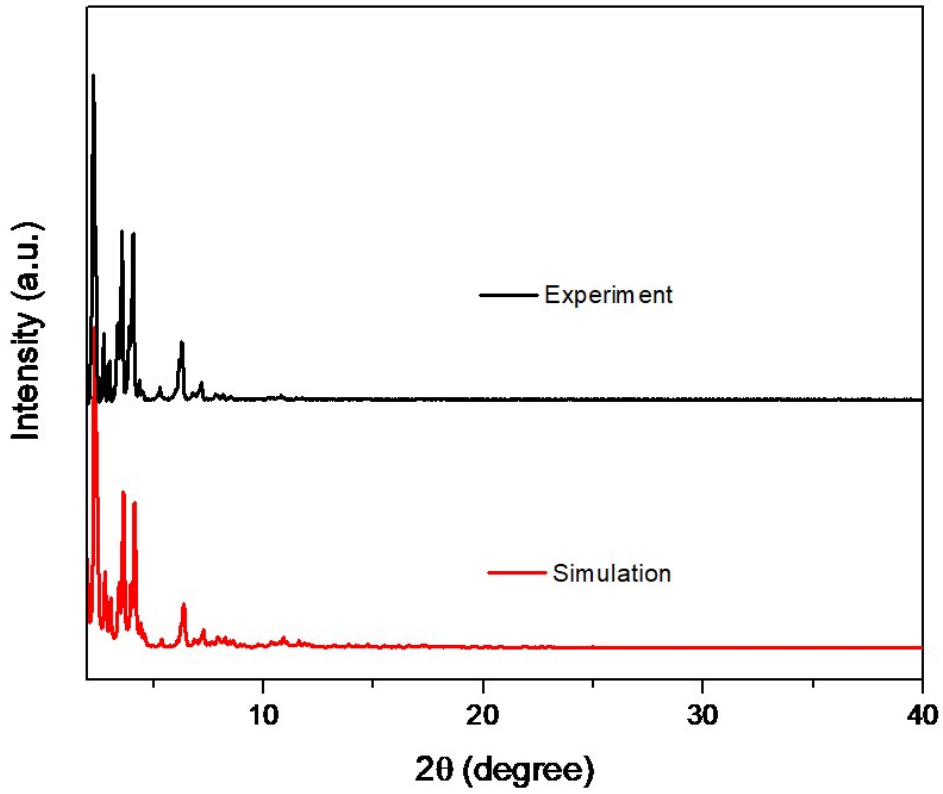


Fig. S3. PXRD patterns of PCN-604 based on simulation (red) and experiment (black).

2. Characterization of PCN-604

Table S1. Porosity comparison between PCN-333 and PCN-604

MOFs	N_2 uptake(cm^3/g)	Pore volume (cm^3/g)	Surface areas (m^2/g)
PCN-333	2490	3.22	4000
PCN-604	1952	3.81	3561

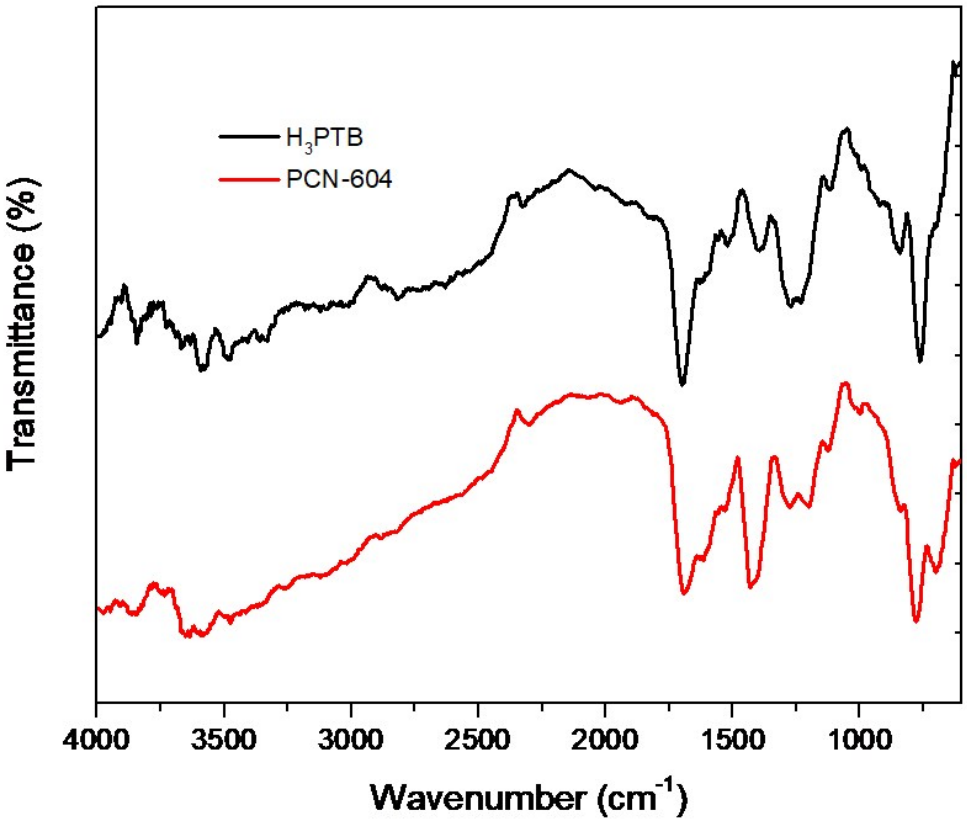


Fig. S4. FT-IR spectra of activated PCN-604 (red) and H_3PTB (black).

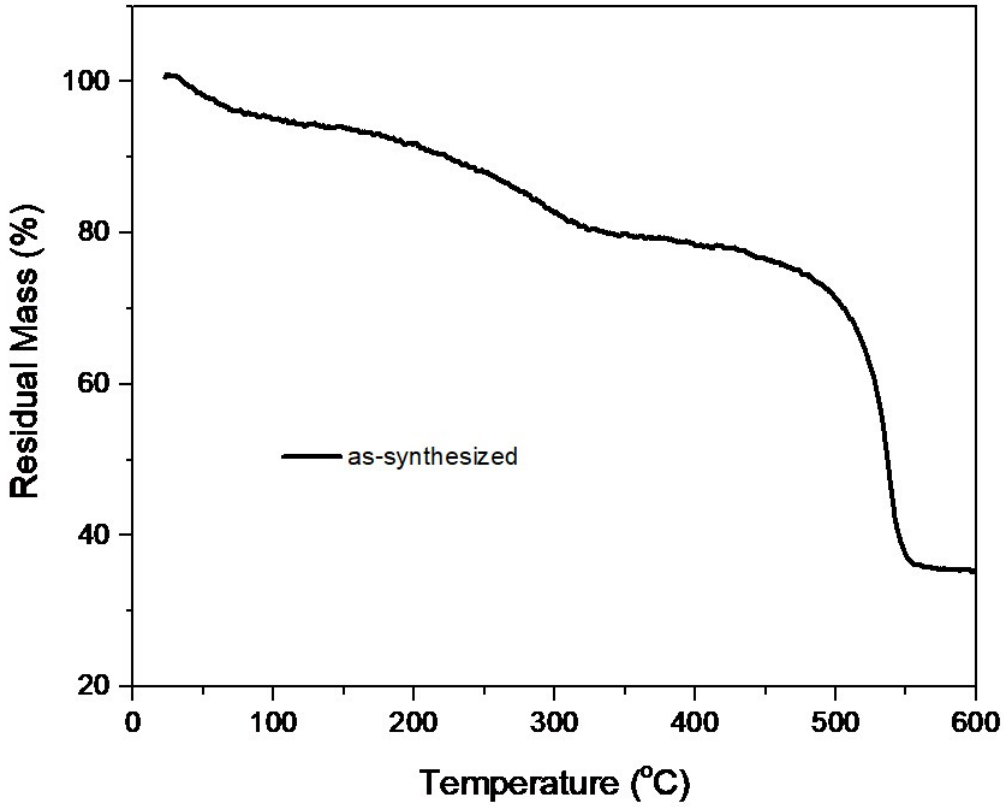


Fig. S5. Thermogravimetric analysis of as-synthesized PCN-604.

3. Chemical stability tests of PCN-604

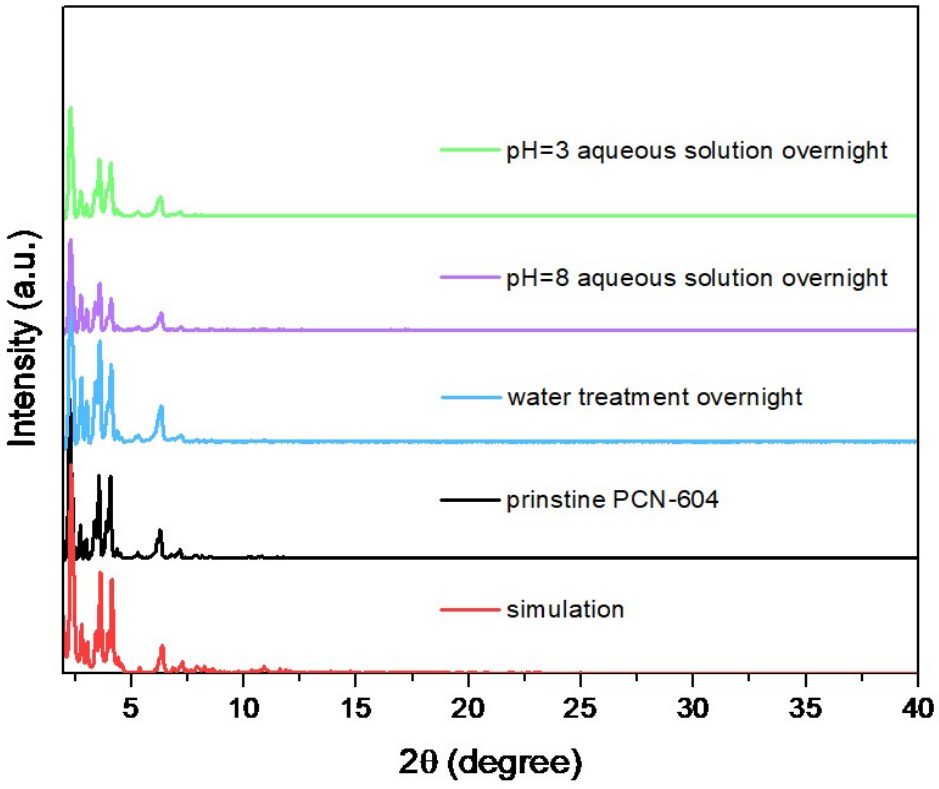


Fig. S6. PXRD patterns of PCN-604 in aqueous solutions with pH values in the range of 3-8.

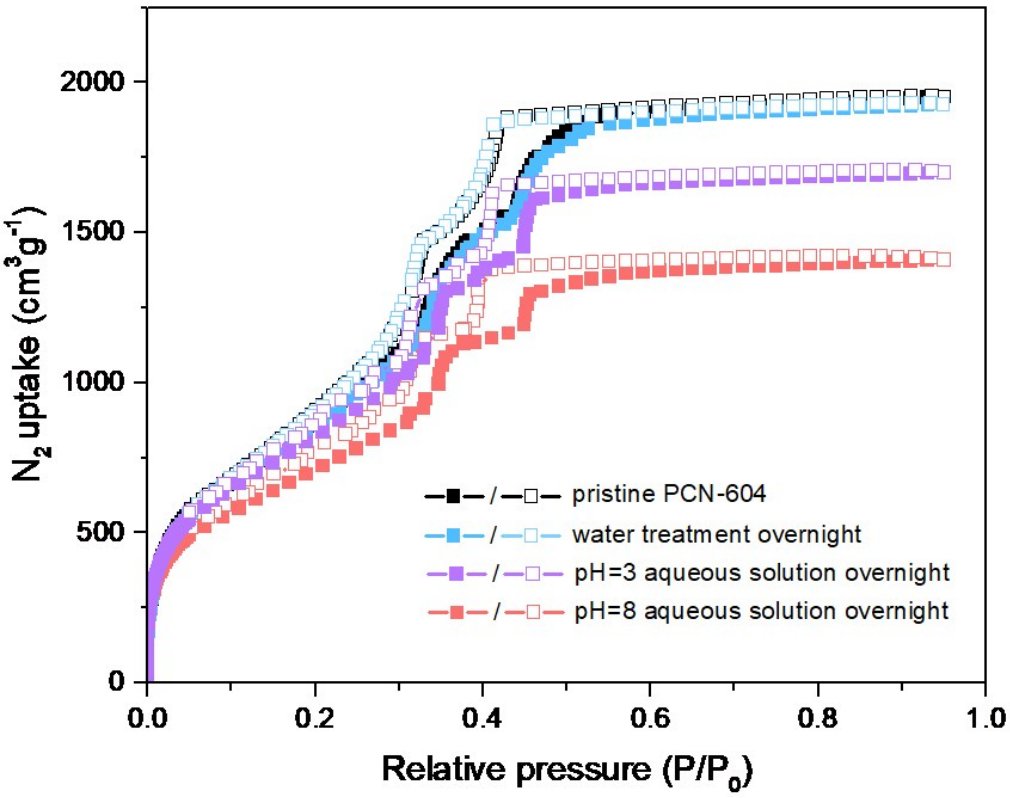


Fig. S7. N_2 uptake isotherms of PCN-604 samples after treatment of aqueous solutions with different pH values.

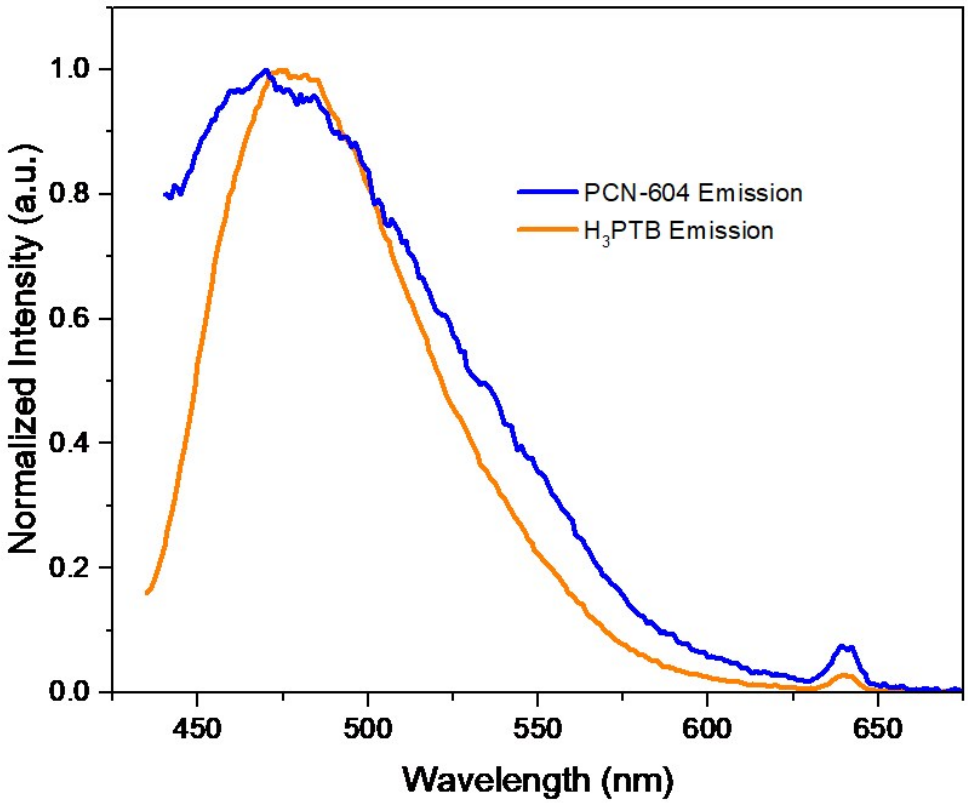


Fig. S8. Normalized Solid-state emission spectra of PCN-604 (blue) and H_3PTB (yellow) upon excitation at 424 nm at room temperature.

4. Photoluminescence Properties

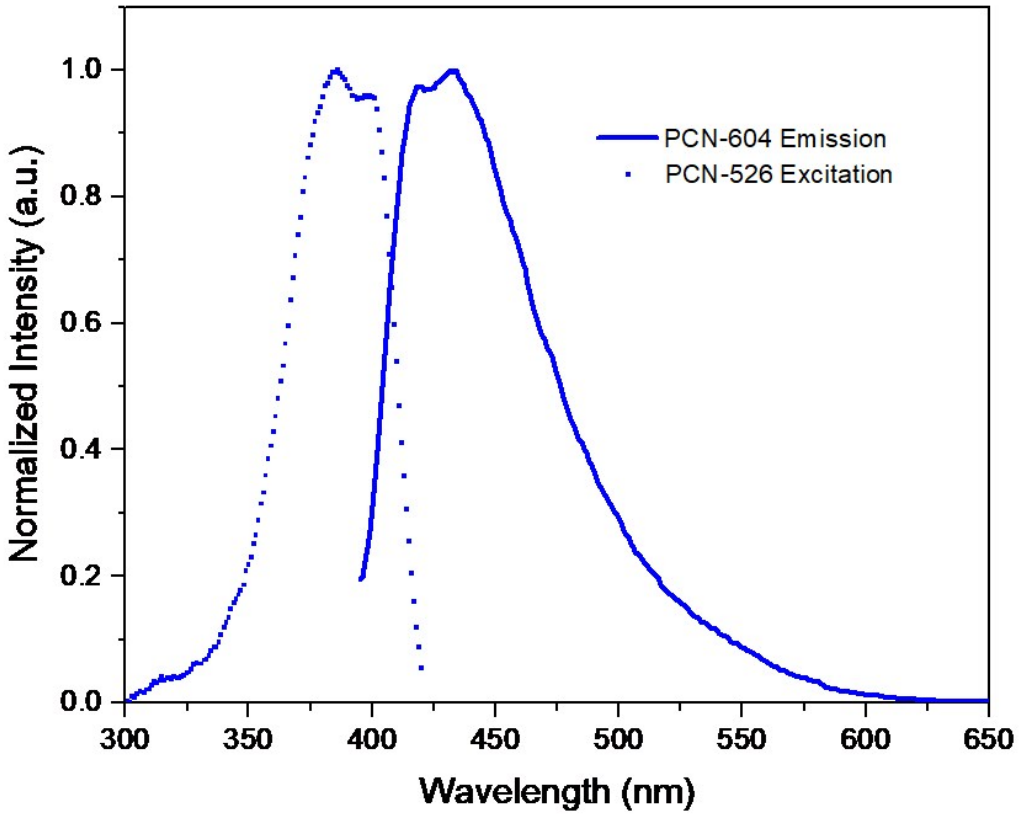


Fig. S9. Solid-state excitation spectrum (blue dot) and emission spectrum (blue line) of PCN-604 at room temperature.

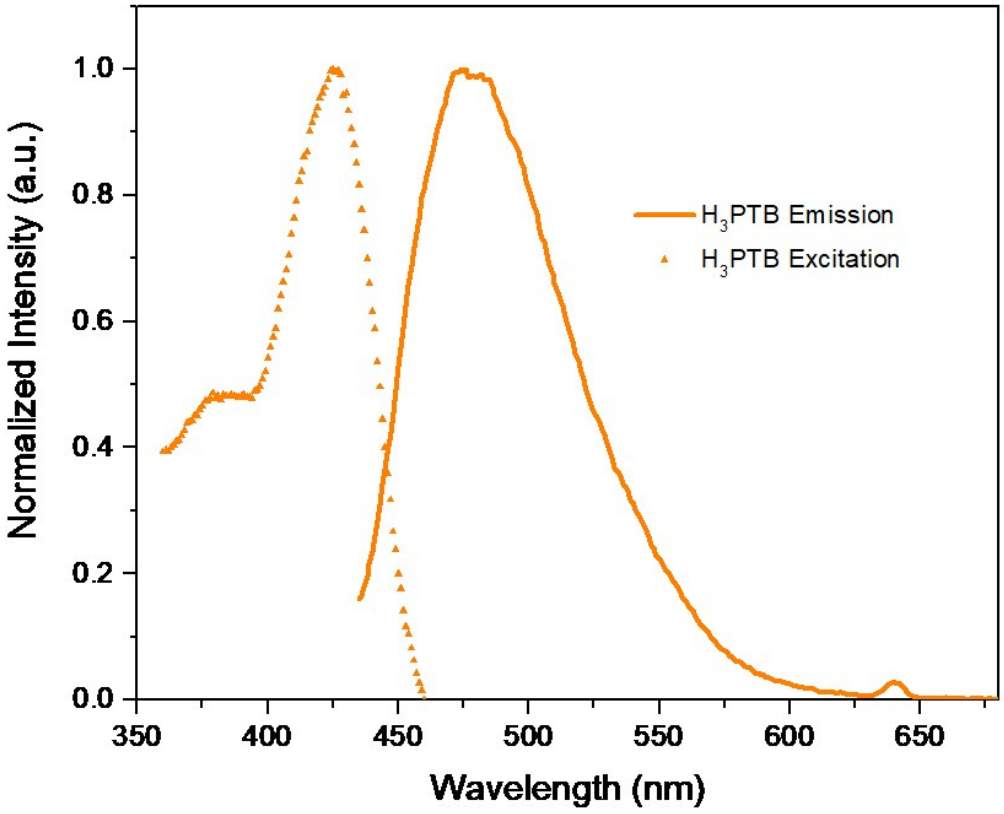


Fig. S10. Solid-state excitation spectrum (yellow dot) and emission spectrum (yellow line) of H_3PTB at room temperature.

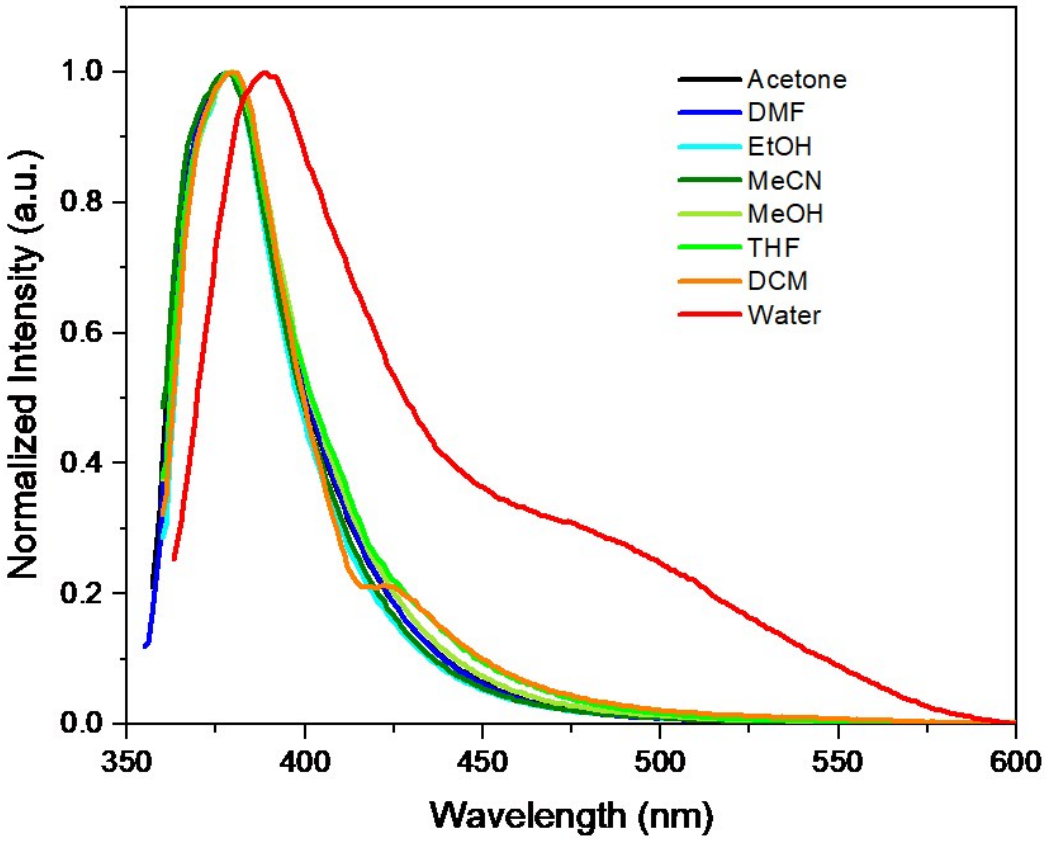


Fig. S11. Emission spectra of PCN-604 suspensions dispersed in various solvents excited at 350 nm.

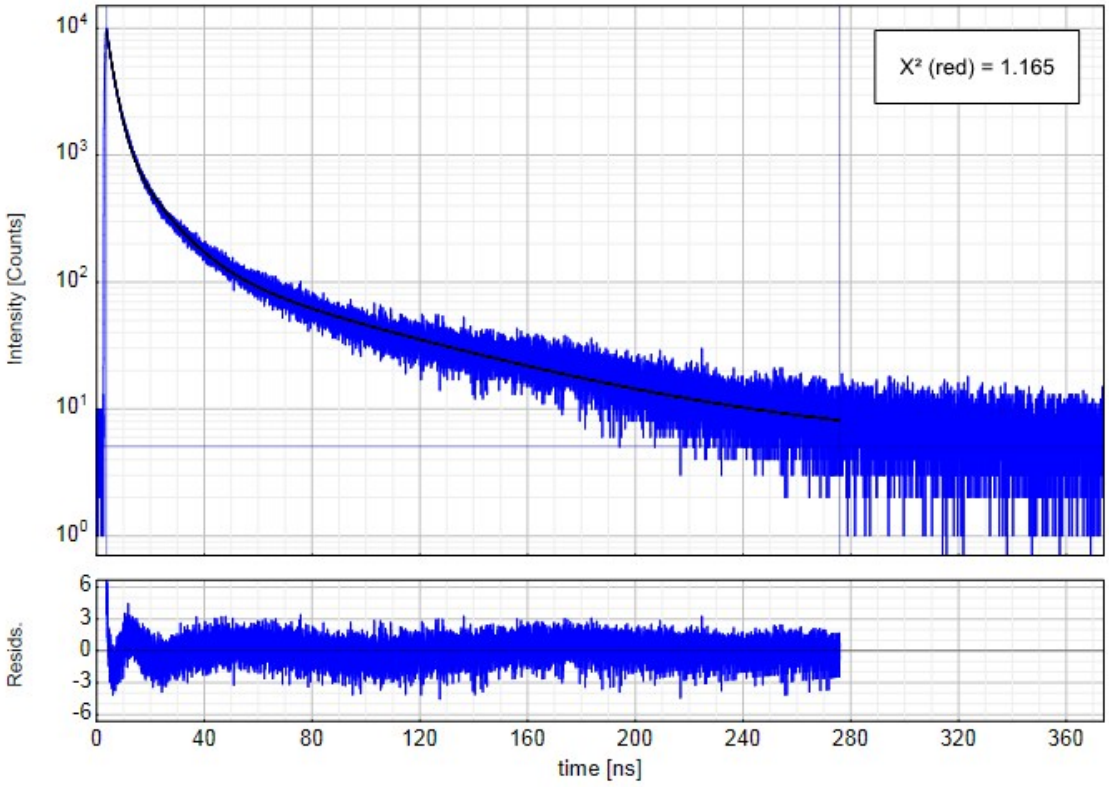


Fig. S12. Fit result of time-resolved fluorescence decay trace of PCN-604 with model decay (black line) and residuals (bottom).

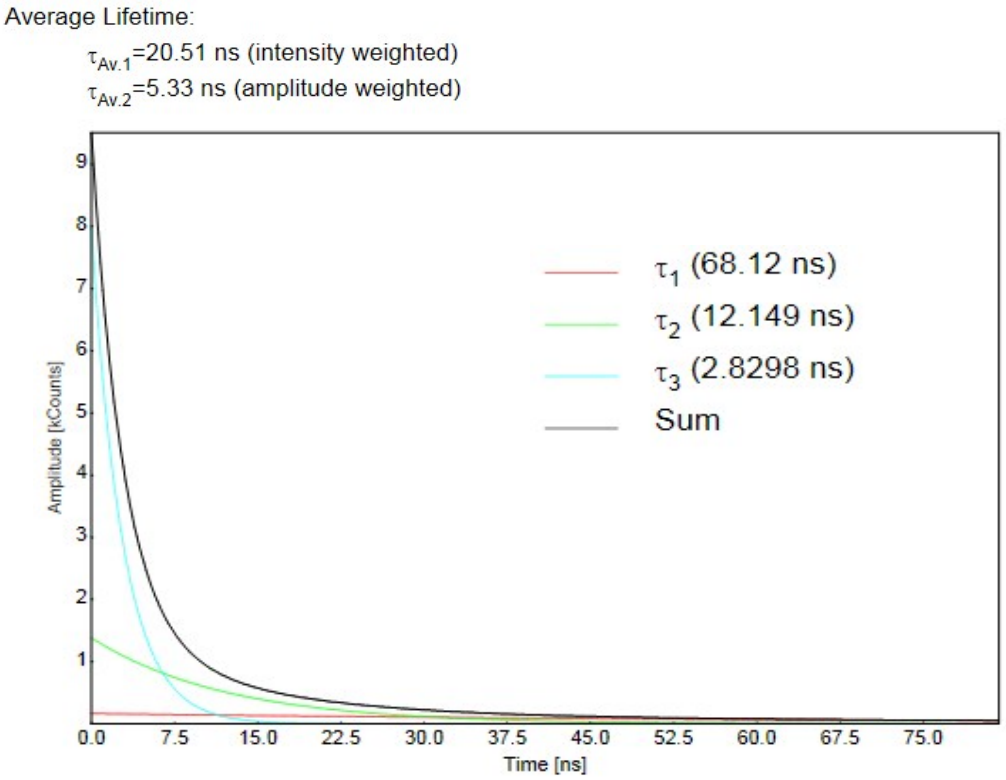


Fig. S13. Fitted decay and exponential components.

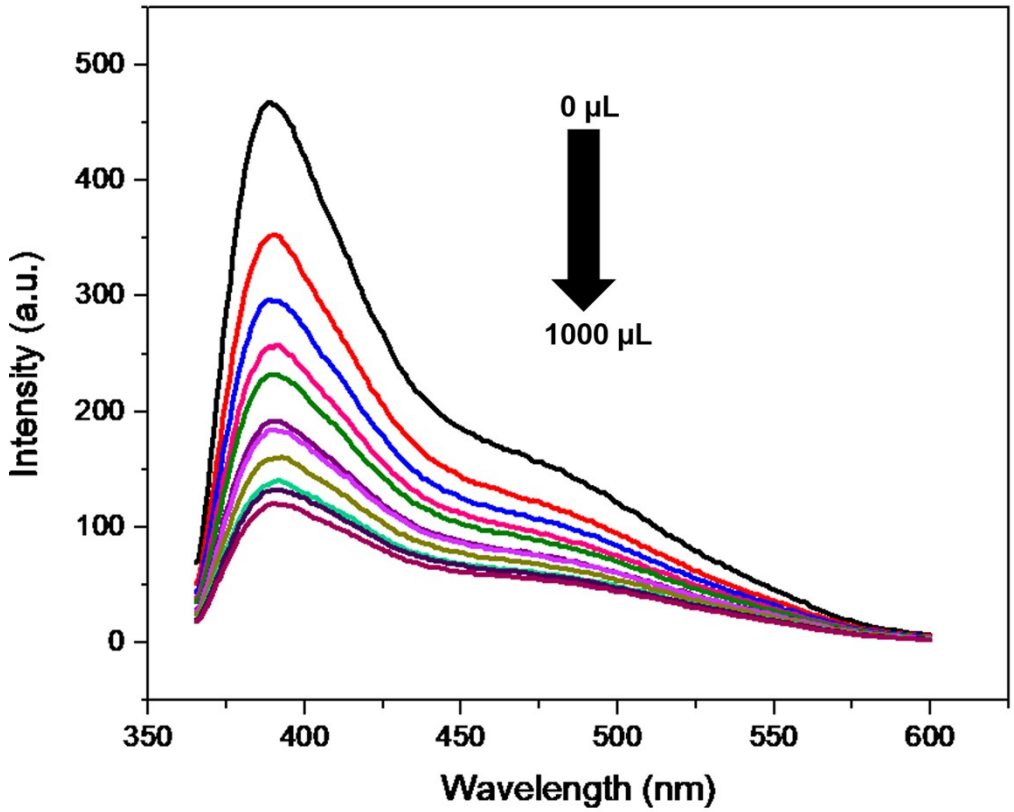


Fig. S14. Fluorescence spectra of PCN-604 suspension in response to different concentrations of Fe^{3+}. Fe^{3+} aqueous solution (1 mM) was added gradually from 20 µL to 1000 µL (20 µL each time).

5. Sensing experiments

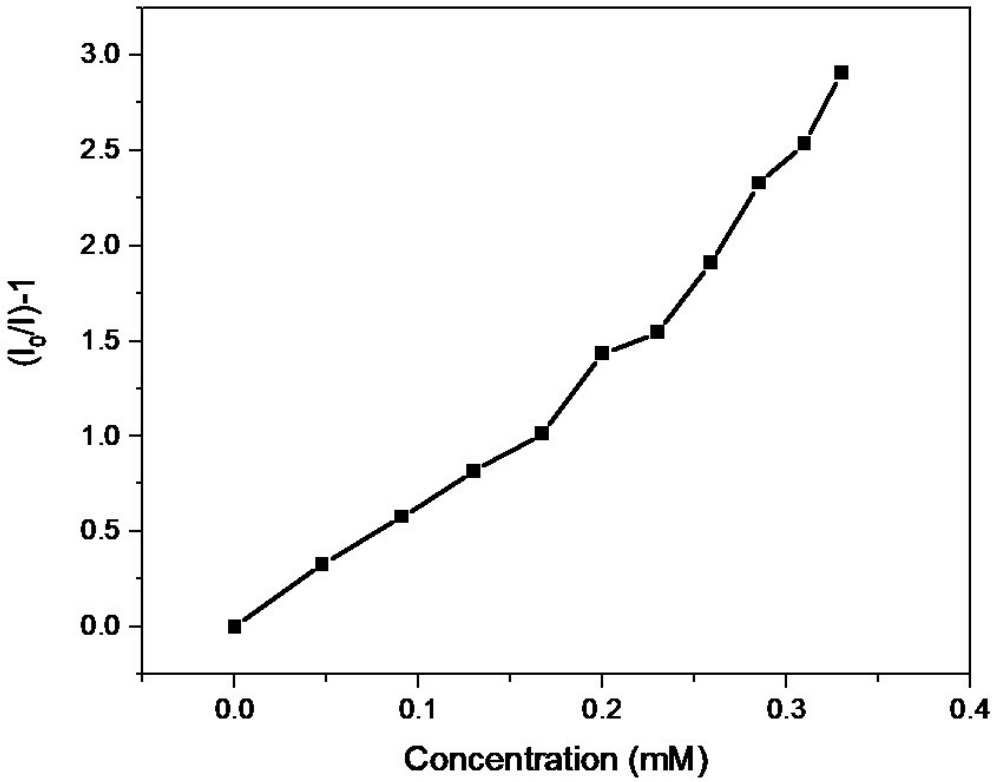


Fig. S15. SV plot of PCN-604.

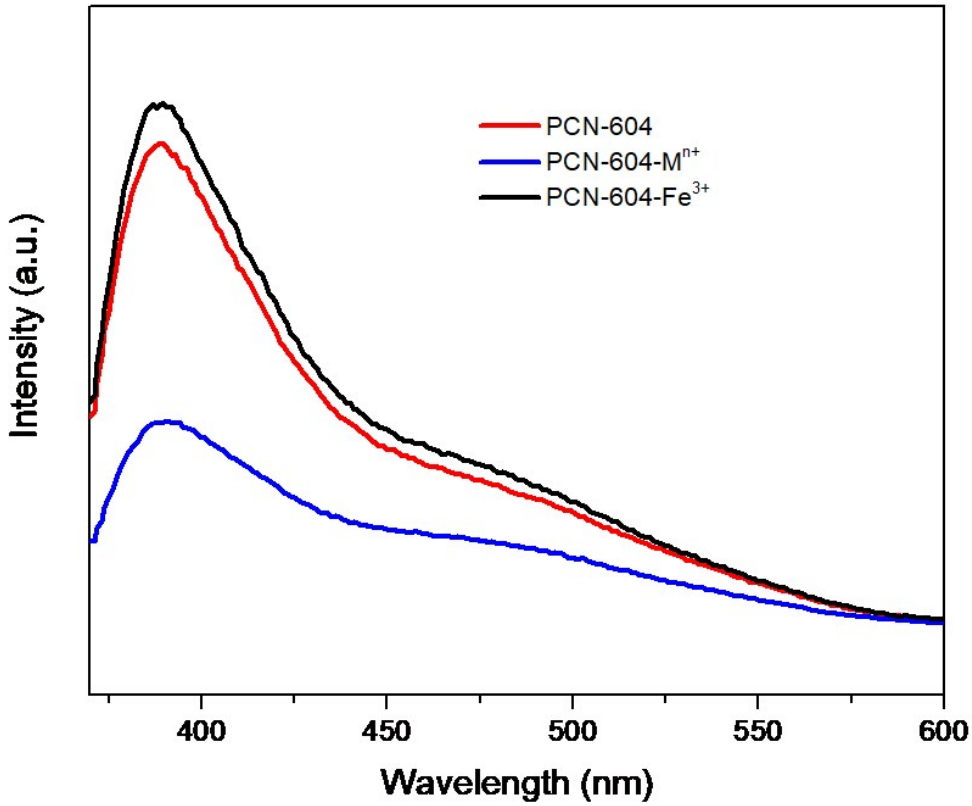


Fig. S16. Fluorescent spectra of original PCN-604 suspension solution, upon addition of 1 mL of 14 metal ions (1 mM for each) and sequent addition of Fe^{3+}(1mM).

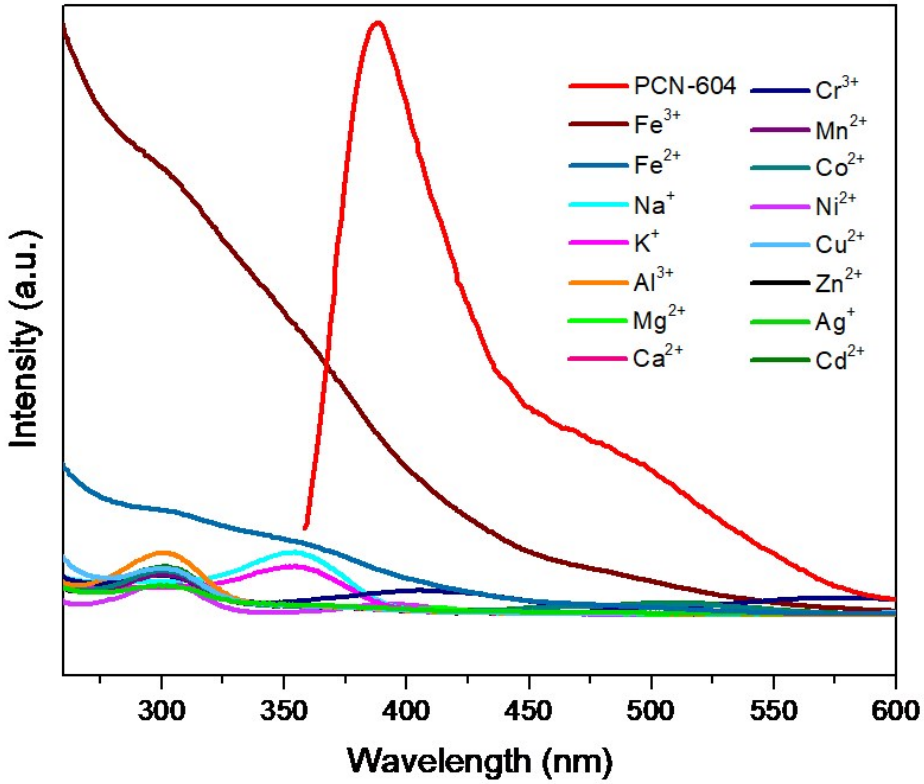


Fig. S17. Emission spectrum of PCN-604 aqueous suspension (red) and absorption spectra of different metal ions solutions in the concentration of 1mM.

Table S2. Comparison of sensing performance of PCN-604 for Fe^{3+} ion with other MOF-based materials.

Materials	Solvent	K_{sv} (M^{-1})	Detection limit (μM)	Ref.
BUT-14	water	2.17 x 10^3	3.8	1
BUT-15	water	1.66 x 10^4	0.8	1
Eu^{3+}@MIL-53-COOH (Al)	water	5.12 x10^3	0.5	2
MIL-53 (Al)	water	-	0.9	3
$Gd_6(L)_3(HL)_2(H_2O)_{10}$ (L = 5,5’ -(pyridine-2,5-diyl)isophthalate)	water	7.89 x 10^2	-	4
Cd-MDIP	water	4.13 x 10^4	0.08	5
EuOHDC	water	-	1.17	6
$[(CH_3)_2NH_2]\cdot[Tb(bptc)]$	ethanol	-	180.1	7
$Eu_2(MFDA)_2(HCOO)_2(H_2O)_6$	DMF	1.58 x 10^3	0.3	8
$(Me_2NH_2)[Tb(OBA)_2]\cdot(Hatz)\cdot(H_2O)_{1.5}$	water	3.4x10^4	-	9
PCN-604	water	8.53 x 10^3	6.2	this work

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