Supporting Information

Reversible Fluorescence Switching of Metal-Organic Framework Nanoparticles for Use as Security Ink and Detection of Pb²⁺ Ions in Aqueous Media

Sada Venkateswarlu,^{†,‡,\$} Anikireddy Seshadri Reddy,^{§,⊥,\$} Atanu Panda,^{†,‡} Debraj Sarkar,[‡] and

Younghu Son, [†] Minyoung Yoon*,^{†,1}

[†]Department of Chemistry, Kyungpook National University, Daegu 41566, Republic of Korea

[‡]Department of Nanochemistry, Gachon University, Seongnam 13120, Republic of Korea

[§]Department of Chemical &, Biological Engineering, Gachon University, Seongnam 13120, Republic of Korea

^IGreen-Nano Materials Research Center, Kyungpook National University, Daegu 41566, Republic of Korea

Present address

[⊥](A. S. R) Department of Chemistry, Akal College of Basic Sciences, Eternal University, Baru Sahib, Sirmour 173101, India

Author Contributions

^{\$}These authors contributed equally to this work. The manuscript was written by all authors and all authors have approved the final version of the manuscript.



Figure S1. (a) XRD pattern and (b-e) TEM images of the NH₂-MIL-125(Ti).

TGA analysis was performed to investigate the thermal stability of the NH₂-MIL 125 framework. Figure S2 (ii) shows that the weight loss occurred in three stages. The initial weight

loss of 1.9% between 35 °C and 100 °C corresponds to decomposition of the methanol guest molecules. The major weight loss of 30.1% occurred between the second and third steps from 110 °C to 382 °C, corresponding to the decomposition of solvent molecules and organic linker. Nearly 10.2% weight loss was detected between 400 °C and 700 °C, which can be attributed to degradation of the MOF framework and production of the TiO₂ precursor. Figure S2(i) shows that, for pure NH₂-H₂BDC, a weight loss of 76.5% occurred from 275 °C to 383.5 °C, attributable to the decomposition of organic functional groups of the ligand, which is two-times more amount compared to the framework ligand. These results reveal that the ligand with the titanium precursor enhanced the MOF stability.



Figure S2. TGA of (i) NH₂-H₂BDC and (ii) NH₂-MIL-125(Ti).



Figure S3. SEM images of (a) NH₂-MIL-125(Ti), (b)NH₂-MIL-101(Al), (c) UiO-66-NH₂, and (d) NH₂-MIL-101(Cr).



Figure S4. XRD patterns of (i) NH₂-MIL-101(Al), (ii) UiO-66-NH₂, and (iii) NH₂-MIL-101(Cr).



Figure S5. PL spectra of NH₂-BDC and NH₂-MIL 125(Ti).

As shown in Figure S6, the PL intensities decreased in acidic medium due to protonation of the amino group; therefore, no charge transitions occurred between the ligand and the Ti oxocluster, which led to fluorescence quenching. Another interesting phenomenon is that, at pH > 6, the PL intensity reached a maximum with a blue shift from 460 nm to 435 nm, indicating that deprotonation of the amine as well as $n-\pi^*$ and $\pi-\pi^*$ transitions occurred between the ligand and the Ti oxo-cluster at neutral pH. This was further confirmed by the ζ potential experiment (Figure S7). The isoelectric point of the NH₂-MIL-125(Ti) framework was between pH 5.5 and 6, i.e., this state of framework exhibited higher PL intensity. Subsequently, NH₂-MIL-125(Ti) nanoplates were irradiated with a UV source for 12 h, and the normalized PL intensity was still higher than 0.85 (Figure S8), indicating high stability without photobleaching, and the stability based on different storage periods were also investigated (Figure S9). The overall results confirmed the durability and stability of the probe in aqueous medium, which plays a major role in economically practical applications.



Figure S6. PL spectra of NH₂-MIL-125(Ti) at various pH ($\lambda_{ex} = 360$ nm).



Figure S7. Zeta potential of NH₂-MIL-125(Ti).



Figure S8. Evolution of PL spectra NH₂-MIL-125(Ti)-UV treatment with time (photo bleaching).



Figure S9. Stability of NH₂-MIL-125(Ti) for different storage time periods.



Figure S10. Metal ion selectivity of NH_2 -MIL-125(Ti). The concentration of each metal ion is 11 nM.



Figure S11. PL spectra of the NH_2 -MIL-125(Ti) in the presence of EDTA at concentrations from 0 to 11 nM.



Figure S12. PL intensity behavior of NH₂-MIL-125 (Ti) in the presence of EDTA.



Figure S13. PL spectra of (i) NH₂-MIL-125(Ti), (ii) NH₂-MIL-101(Al), (iii) UiO-66-NH₂, and (iv) NH₂-MIL-101(Cr).



Figure S14. Solid state UV-Vis spectra Kubelka–Munk plot for (i) NH₂-H₂BDC, (ii) NH₂-MIL-125(Ti), (iii) NH₂-MIL-101(Al), (iv) NH₂-MIL-101(Cr), (v) UiO-66-NH₂, and (vi) TiO₂ NPs.



Figure S15. SEM images of (a) paper, particles on a paper (b, c) NH₂-MIL-125(Ti).

Fluorescence lifetime (τ) of NH₂-MIL-125 (Ti) was calculated and the average lifetime of the framework was 9.5 \pm 0.25 ns ($\chi^2 \sim 1.1$), in good agreement with reported values (Figure S16, Table S1).^{S1} The NH₂-MIL-125(Ti) MOF was also applied for the detection of Pb²⁺ ions in real water samples (Figure S17 and S18, Table S2 and S3). The detection limit signified an ultrasensitive performance (152 and 186 pM).



Figure S16. Time traces of NH₂-MIL-125(Ti) and NH2-MIL-125(Ti)-Pb²⁺ in water.



Figure S17. Pb^{2+} ion detection in tap water.



Figure S18. Pb^{2+} ion detection in river water.

Table S1. Lifetime decay values of NH2-MIL-125(Ti) and NH2-MIL-125(Ti)-Pb²⁺

S. No.	χ^2	τ_1 (ns)	$\tau_2(ns)$
MOF	1.122	0.1	9.6
MOF-Pb ²⁺	0.998	0.018	0.85

Table S2. Limits of detection of Pb^{2+} ions

S. No	Fluorescence Probe	LOD (pM)
1	MOF-Pb ²⁺	7.7
2	MOF-Pb ²⁺ River water	186
3	MOF-Pb ²⁺ Tap water	152

Table S3. Spiked values of NH₂-MIL-125(Ti) with Pb^{2+} ions

Sample	Spiked Pb ²⁺ [nM]	Found [nM]	Recovery (%)	RSD (%)
River water	1	0.952	95.21	1.00
	2	1.969	98.45	0.28
	3	3.026	100.86	0.24
	4	3.972	99.32	1.11
	5	5.036	100.72	0.20
	6	5.985	99.75	0.70
Tap water	1	0.985	98.50	3.95
	2	2.045	102.2	0.79
	3	2.977	99.23	0.10
	4	4.096	102.4	0.15
	5	4.912	98.24	0.10
	6	5.975	99.58	0.06

References

S1 Nasalevich, M. A.; Hendon, C. H.; Santaclara, J. G.; Svane, K.; Linden, B. V.; Veber, S. L.; Fedin, M. V.; Houtepen, A. J.; Veen, M. A. V.; Kapteijn, F.; Walsh, A.; Gascon, J. Electronic Origins of Photocatalytic Activity in d⁰ Metal Organic Frameworks. *Sci. Rep.* 2016, *6*, 23676-23684.