Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

MOF-5 Fortified Fiber Optic Plasmonic Absorption-based Pb(II) Ion Sensor for Rapid Water Quality Monitoring

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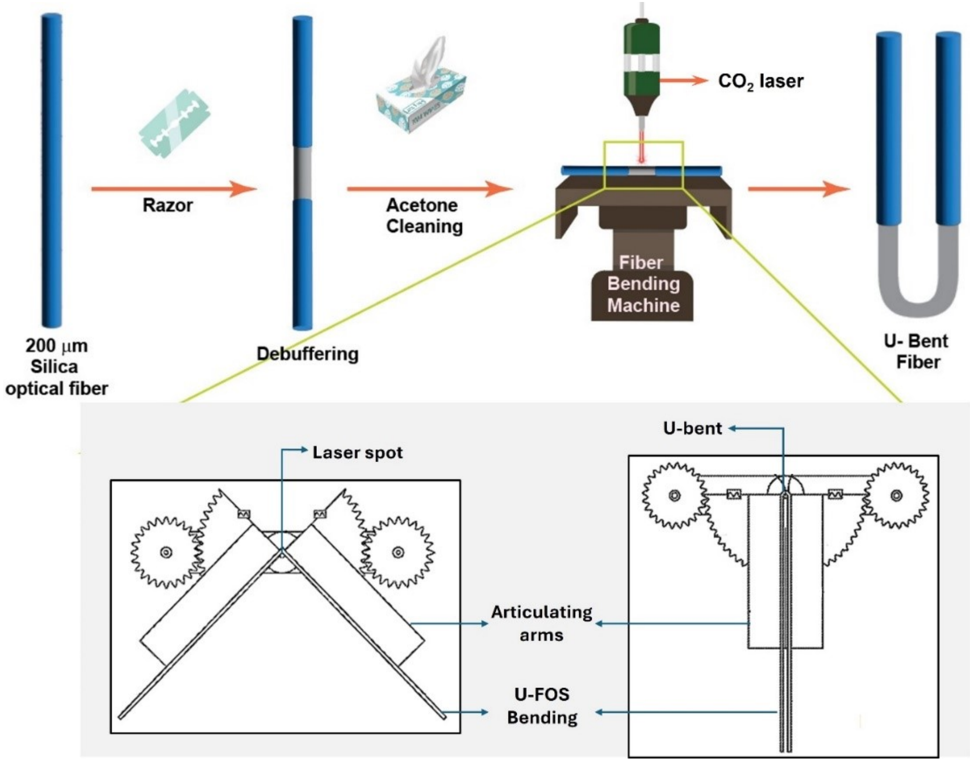


Figure S1. Schematic showing the articulating arm-based mechanism for the fabrication of U-bent fiber optic sensor (U-FOS). The arms will be horizontal to accommodate a straight debuffered/decladded fiber in the initial position. Then the fiber core is continuously illuminated with a laser radiation to melt it and the articulating arms are displaced as shown above to obtain a U-bent probe [US Patent US20220332628A1 filed on date 2020-11-16].

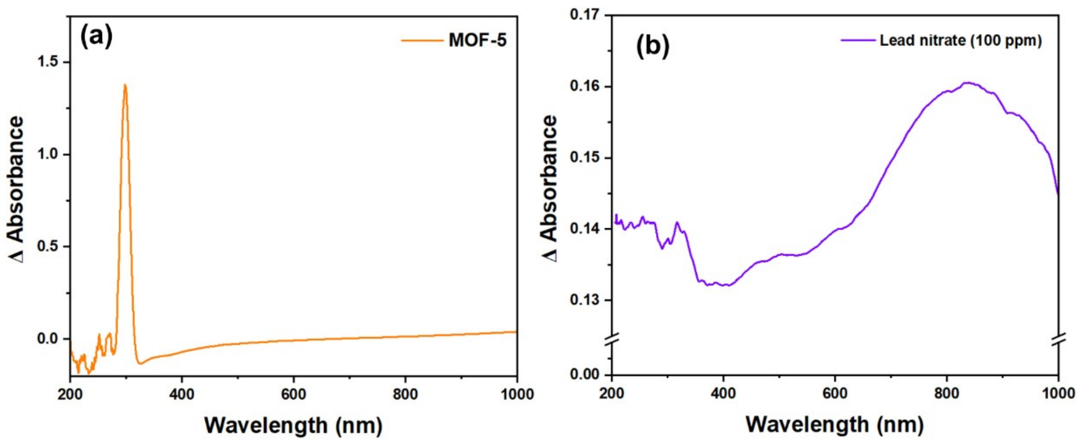


Figure S2. UV-vis spectra of **(a)** MOF-5 growth solution **(b)** [100 ppm] Pb (II) ion solution using UV-vis spectrophotometer.

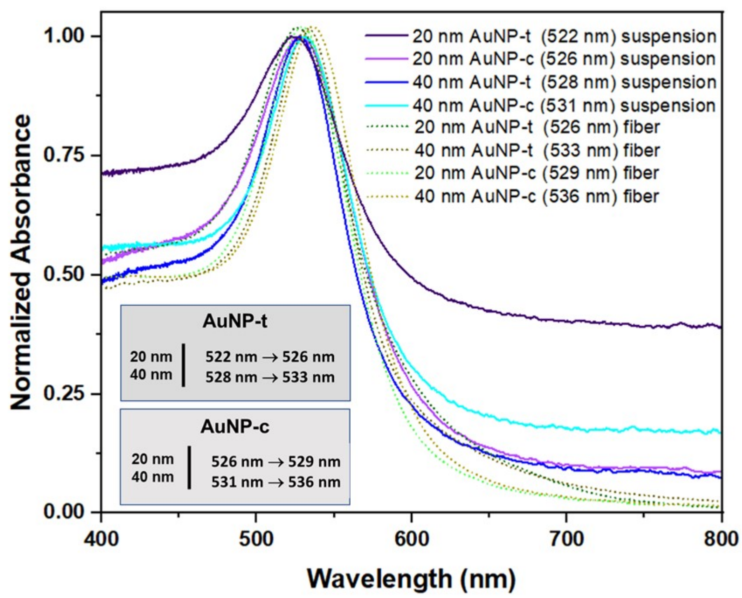


Figure S3. Absorbance spectra obtained from AuNP in suspension and on FOS probes (dotted) for the various AuNP suspensions tested for realizing PACS.

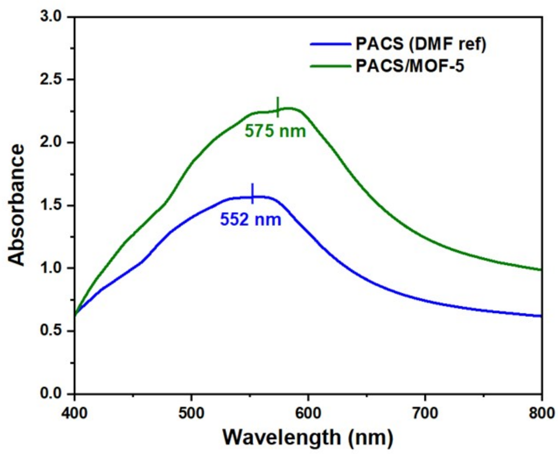


Figure S4. EWA spectra of bare PACS and PACS/MOF-5 probes in DMF.

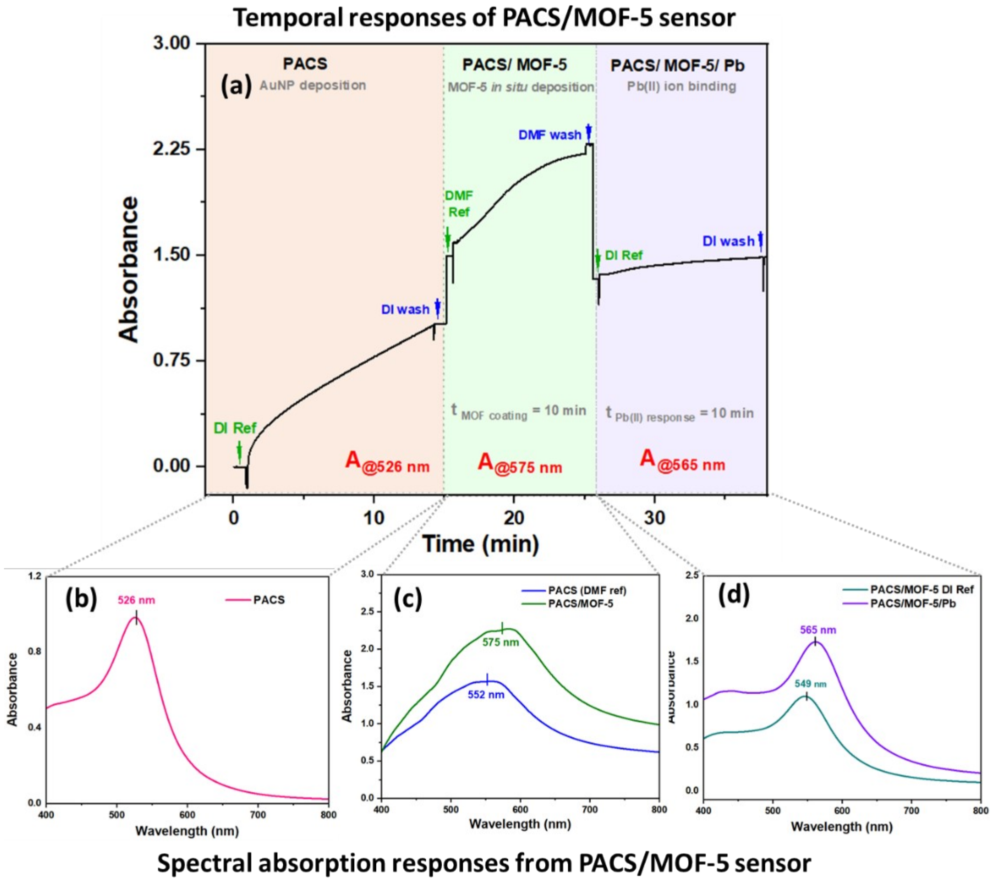


Figure S5. MOF-5 coated U-FOS fabrication steps: **(a)** Online monitoring of the time-absorbance response during AuNP-t, MOF-5, and Pb(II) binding on the U-FOS. The spectral absorptions of the corresponding binding responses are shown in **(b-d)**, The EWA spectra of **(b)** AuNP-t bound silanized U-FOS (with DI reference) **(c)** DMF reference (blue) and subsequent PACS/MOF-5 (green) **(d)** DI reference (green) and Pb(II) bound PACS/MOF-5.

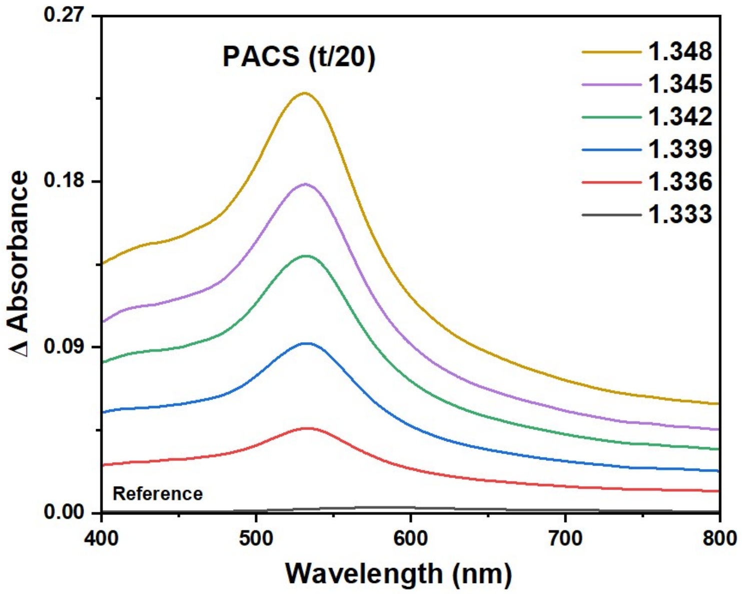


Figure S6. Absorption spectra obtained from PACS probes to various sucrose solutions (RI = 1.333 to 1.348)

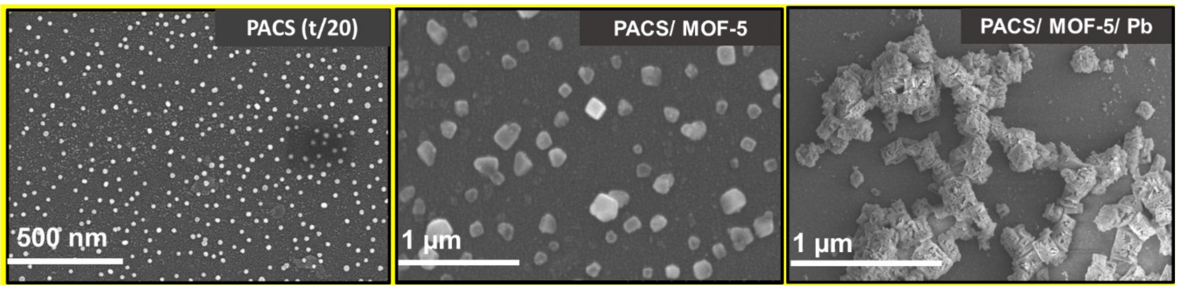


Figure S7. SEM micrographs of the sensor probes. **(a)** silanized U-FOS with 1 arb unit of AuNP-t/20 (after wash) **(b)** bare PACS probe exposed to MOF-5 growth solution for 10 min and washed; **(c)** PACS/MOF-5 probe exposed to 10 ppm of Pb(II) ion solution.

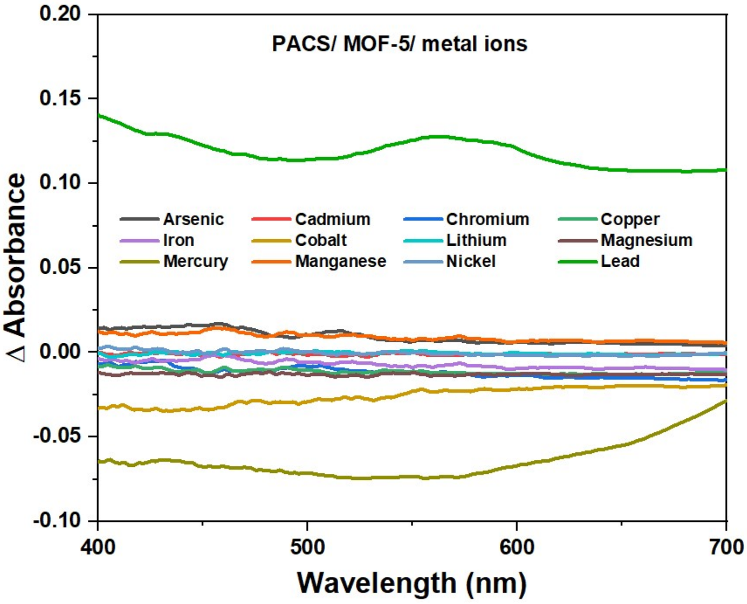
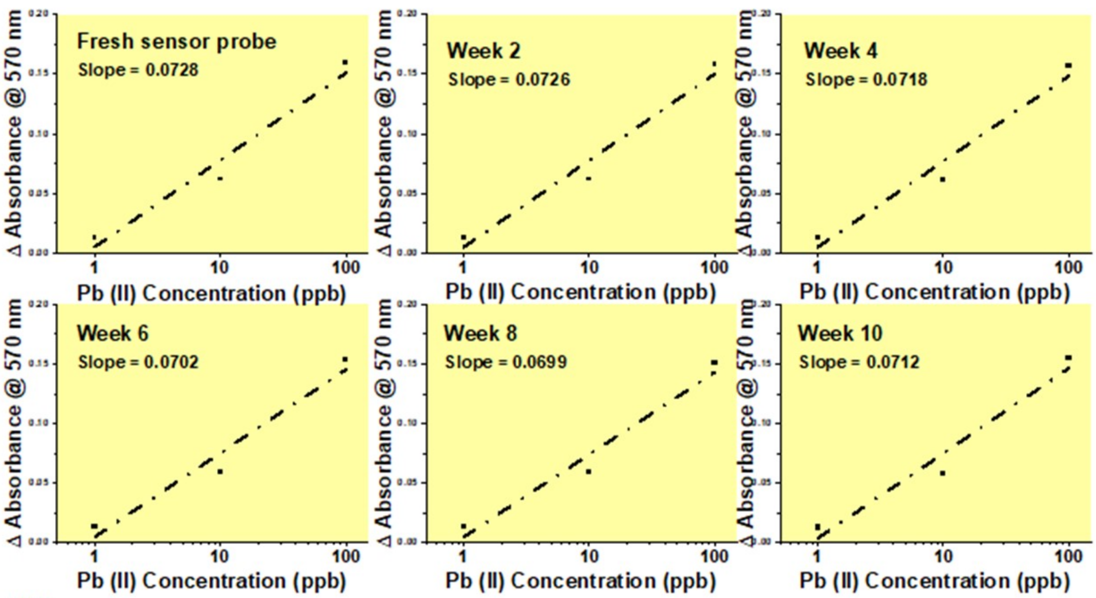
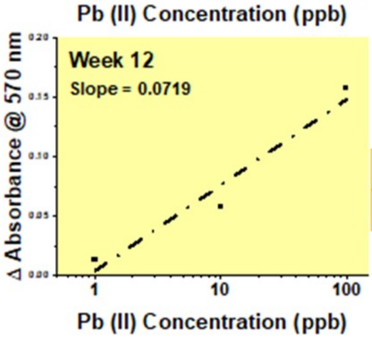


Figure S8. Spectral absorption responses from PACS/MOF-5 probes subjected to 50 ppm of potential interfering metal ions and 1 ppm of Pb(II) ions. [Note: Interaction of Hg(II) ions with the sensor probes resulted in spectral changes in the negative scale, pointing to potential desorption of MOF-5 from the sensor].

Figure S9. Photographic images of the leachate sample collected from various dumpsites.





% variation with respect to the fresh probes

Week 2	Week 4	Week 6	Week 8	Week 10	Week 12
0.301908	1.344861	3.636613	4.062028	2.209414	1.20763

Figure S10. Shelf-life sensitivity of PACS/MOF-5 probes: The sensitivity responses obtained every 2 weeks, by exposing the sensor probes to 1, 10, and 100 ppb of Pb(II) ion concentrations.

Table S1. Commercially available field sensors for lead ion detection (Dore et. al 2020)*

Field Analyzer	**[#]ASV-1**	**ASV-2**	**ASV-3**	**ASV-4**	**[@]Color-1**	**Color-2**	**Fluorescence**
Manufacturer	Palintest	Metrohm	$Trace_2O$	Modern water	Hach	Industrial Test Systems	ANDalyze
Pb Concentration range (µg/L)	2–100	0.2–Not specified	5–500	0.5–800	5–150	3–500	2–100
Sample prep & analysis Time	<5 min	<5 min	<5 min	<15 min	~12 min	<5 min	<5 min
Precision	1 ppb	Not specified	Not specified	Not specified	Not specified	Not specified	± 15% or 2 ppb
Sample volume Processed (Analyzed)	5 mL (5 mL)	15 mL (15 mL)	Not specified	10 mL	100 mL (10 mL)	50 mL (4 mL)	5 mL (1 mL)
# of steps for analysis	3 (Low)	Not specified (High)	Not specified (High)	9 (Moderate)	20 (High)	7 (Low)	6 (Low)
Relative capital cost ($, $$, $$$, $$$$)	$$	$$$	$$$	$$$	$	$	$$
Capability to measure other metals	Cu	As, Hg, Cu	As, Cd, Cr, Cu, Mn, Hg, Ni, Zn	Zn, Cd	No	Hg, Cd	Cu, U, Hg, Cd, Zn
Wastes generated	Mercury electrode (hazardous)	Not specified	Not specified	Not specified	Not specified	Not specified	Non-hazardous

*Adapted, Doré, E.; Lytle, D. A.; Wasserstrom, L.; Swertfeger, J.; Triantafyllidou, S. Field Analyzers for Lead Quantification in Drinking Water Samples. Crit. Rev. Environ. Sci. Technol. 2021, 51 (20), 2357–2388. https://doi.org/10.1080/10643389.2020.1782654.

[#]ASV – Anodic stripping voltammetry; [@]Color – Colorimetry

Table S2. Comparison of the selectivity efficacy and ease of PACS/MOF-5 fabrication with that of the reported optical techniques (in **Table 3**)

Selectivity				**Ease of fabrication**		**Ref**
No. of ions tested	$X = \frac{[HMI]}{[Pb(II)]}$	$\frac{Max\,[HMI]\,Response}{[Pb(II)]\,Response} \times \frac{1}{X} \times 100$	Score	Sensor fabrication/ Ease of instrumentation	Receptor synthesis	
14	50	1.88	+++	+	++	52
8	1	7	+++	++	+	53
8	1	35.71	++	+	+	54
12	1	54.5	+	++	+++	55
5	1	30.76	++	+++	++	35
5	1	400	+	+++	+++	33
-	-	-	-	+++	++	34
9	1	51.22	+	+++	+++	32
6	1	32.5	++	+++	+++	36
11	100	0.086	+++	++	+++	56
11	50	0.25	+++	+++	+++	This work

Ease of Fab: very difficult = + difficult = ++ easy = +++
Selectivity: <10= +++, <50 = ++ , >50 = +

Section A: Highlights of the current study's novel findings

- Stable MOF-5 coated FOS using stronger coordination bonds of MOF-5 to FOS via AuNP-t were developed, in comparison to the physiosorbed MOF coatings adopted in previous articles in the literature.
- Detailed optimization and characterization studies towards the development of MOF-5 based plasmonic Pb(II) ion sensor were presented, where the influence of the AuNP capping agent on the MOF-5 deposition and AuNP size on the sensor sensitivity was demonstrated for the first time.
- Deposition parameters including precursor concentrations and deposition time were optimized for the *in-situ* MOF-5 deposition over the AuNP bound to FOS probes at room-

temperature by adopting the addition of triethylamine, unlike the conventional high-temperature protocols, so that the online monitoring and optimization steps are possible with ease.

- A variety of functionalized MOF-5 are the widely reported MOFs for Pb ion detection and removal. However, a simpler pristine MOF-5 was chosen for highly selective and sensitive Pb ion detection, and a synthesis route for an *in-situ* deposition of MOF-5 over the AuNP was established.
- FOS system offers a variety of advantages in comparison to the conventional colorimetric, and fluorescence techniques for HMI detection, as briefly discussed in the introduction.
- Refractive index-based optical transduction technique utilized in this study quantifies the morphological changes in the MOF-5 receptors in real-time while interacting with Pb(II) ions. The enhanced sensing technique using a plasmonic FOS utilized here permits a sensitive online monitoring of the sensor signal, while MOF-5 receptor permits selective detection. Here, the RI changes in MOF-5 matrix were detected in terms of plasmonic characteristic changes in the AuNP using the EWA phenomenon of U-FOS probes, unlike the Cr(VI) and Cu(II) ion sensors developed in our previous studies, where the direct RI-based changes were measured in terms of the optical losses in the U-FOS.
- In comparison to the available recent Pb ion detection studies, the proposed sensor exhibits a better performance in terms of sensor parameters such as selectivity, sensitivity, and dynamic range.
- In addition, these sensors are stable over 3 months (shelf life). The developed sensor was also validated with ICP-MS for the leachate water sample data.