

Supporting information

Machine learning-driven sensor array based on luminescent metal-organic frameworks for simultaneous identification of multiple anions in environmental waters

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Fig. S13. Machine learning-supported fluorescent sensor array for the identification of five anions in tap water samples. (a) Heatmaps of randomly divided training sets ($n=60$) and test sets ($n=24$). (b) Schematic of ANN algorithm for five anions in tap water samples. Comparison of (c) training set predicted results and (d) test set predicted results. Confusion matrix for (e) training data and (f) test data.

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Table S5. Identification of blind samples with five anions spiked in tap water.

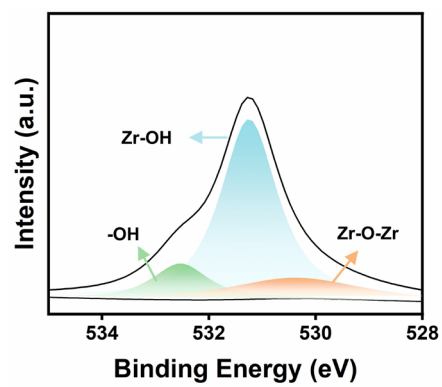
Table S6. Identification of blind samples with five anions spiked in lake water.

Reagents and Chemicals

N,N-dimethylformamide (DMF), benzoic acid, acetone, zirconium(IV) chloride, 2,5-diaminoterephthalic acid, 2,5-dihydroxyterephthalic acid, acetic acid were obtained from Maclean Biochemical Technology Co. (Shanghai, China). ClO_4^- , F^- , NO_3^- , PO_4^{3-} , SO_4^{2-} were obtained from Zhenjiang Dewei Chemicals Co. (Zhenjiang, China). All other chemicals and solvents were of analytical grade or of the highest purity available. All solutions were prepared using deionized water.

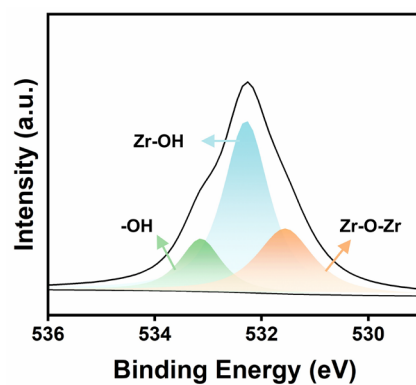
Instrumentation

Fluorescence spectra were recorded on a Thermo Lumina fluorescence spectrophotometer (Thermo, USA). UV-visible (UV-vis) absorption spectra were recorded on a UV-2600 scanning spectrophotometer using a 1 cm quartz cuvette (Shimadzu, Japan). The particle size was analyzed using a JEM 2100 Transmission Electron Microscopy (TEM) (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250 XI electron spectrometer (Thermo, USA). FT-IR spectra were obtained using a 16 Bruker IFS66V FT-IR spectrometer (Germany). The hydrodynamic sizes were investigated using a dynamic light scattering (DLS) spectrophotometer (Malvern Zetasizer NanoZS, UK). The collected data matrixes were treated with hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) using SPSS (version 26.0).



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94 **Fig. S1.** O 1s spectrum of UiO-66-NH₂.



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96 **Fig. S2.** O 1s spectrum of UiO-66-OH.

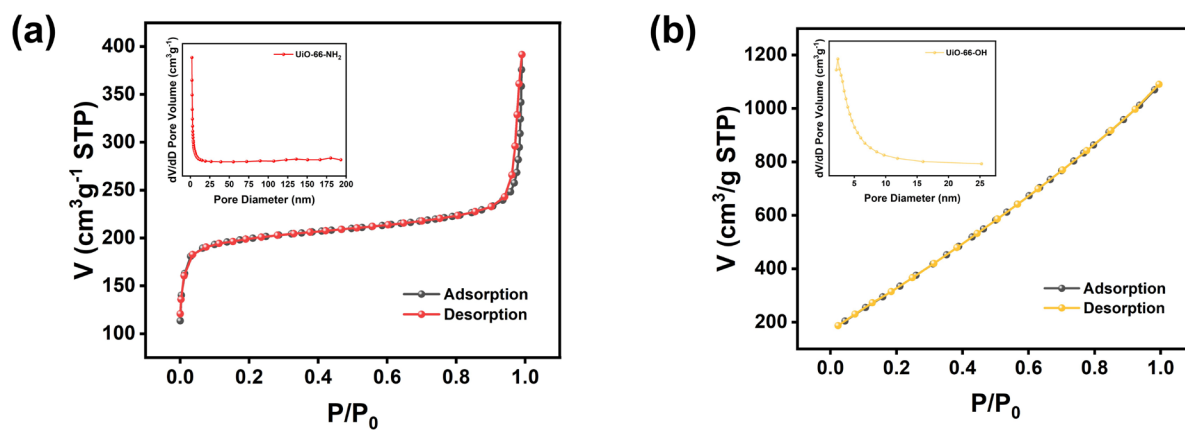


Fig. S3. Nitrogen adsorption/desorption isotherms and pore size distributions of (a) UiO-66-NH₂ and (b) UiO-66-OH.

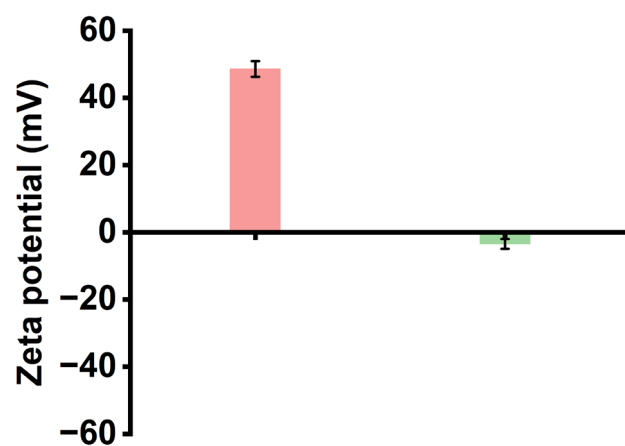


Fig. S4. Zeta potentials of UiO-66-NH₂ and UiO-66-OH.

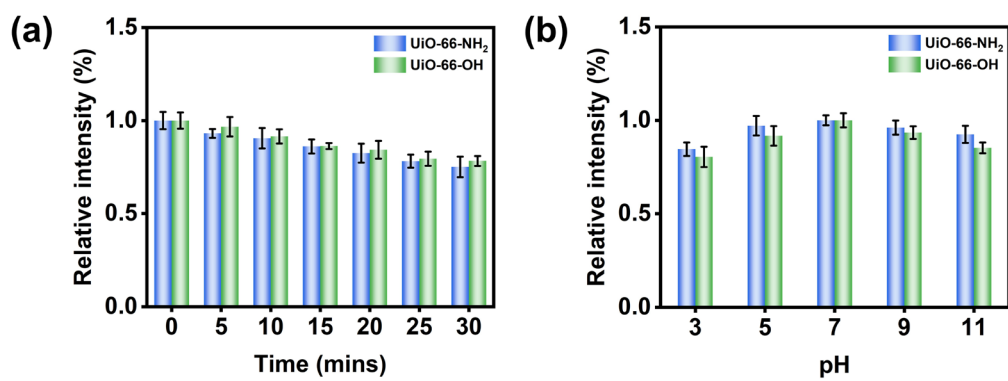


Fig. S5. Stability of UiO-66-NH₂ and UiO-66-OH under UV irradiation and different pH.

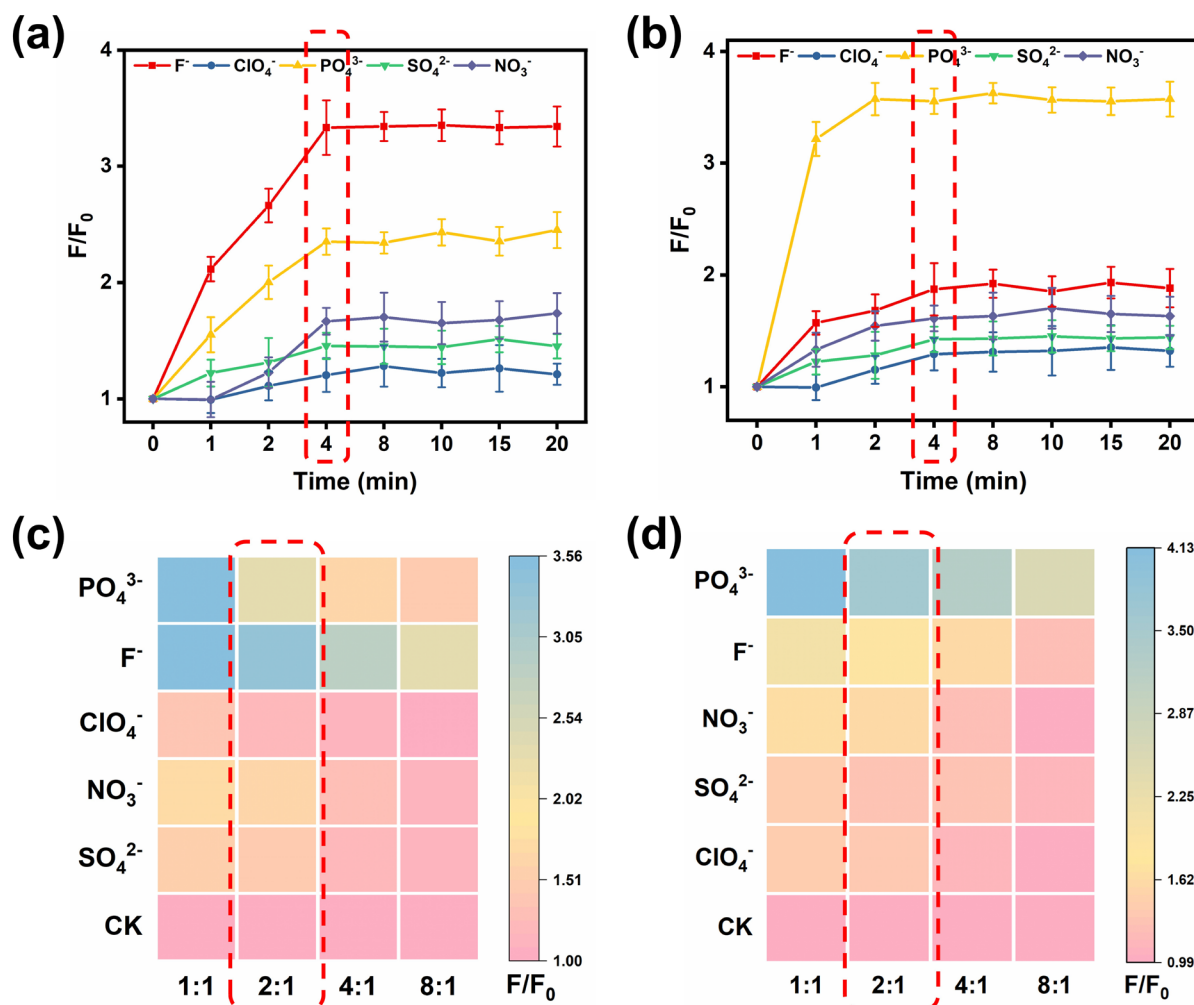


Fig. S6. Optimization of the fluorescence array sensor based on UiO-66-NH₂ and UiO-66-OH for the detection of five anions. Reaction time for (a) UiO-66-NH₂ and (b) UiO-66-OH. The ratio of probe and anions for (c) UiO-66-NH₂ and (d) UiO-66-OH.

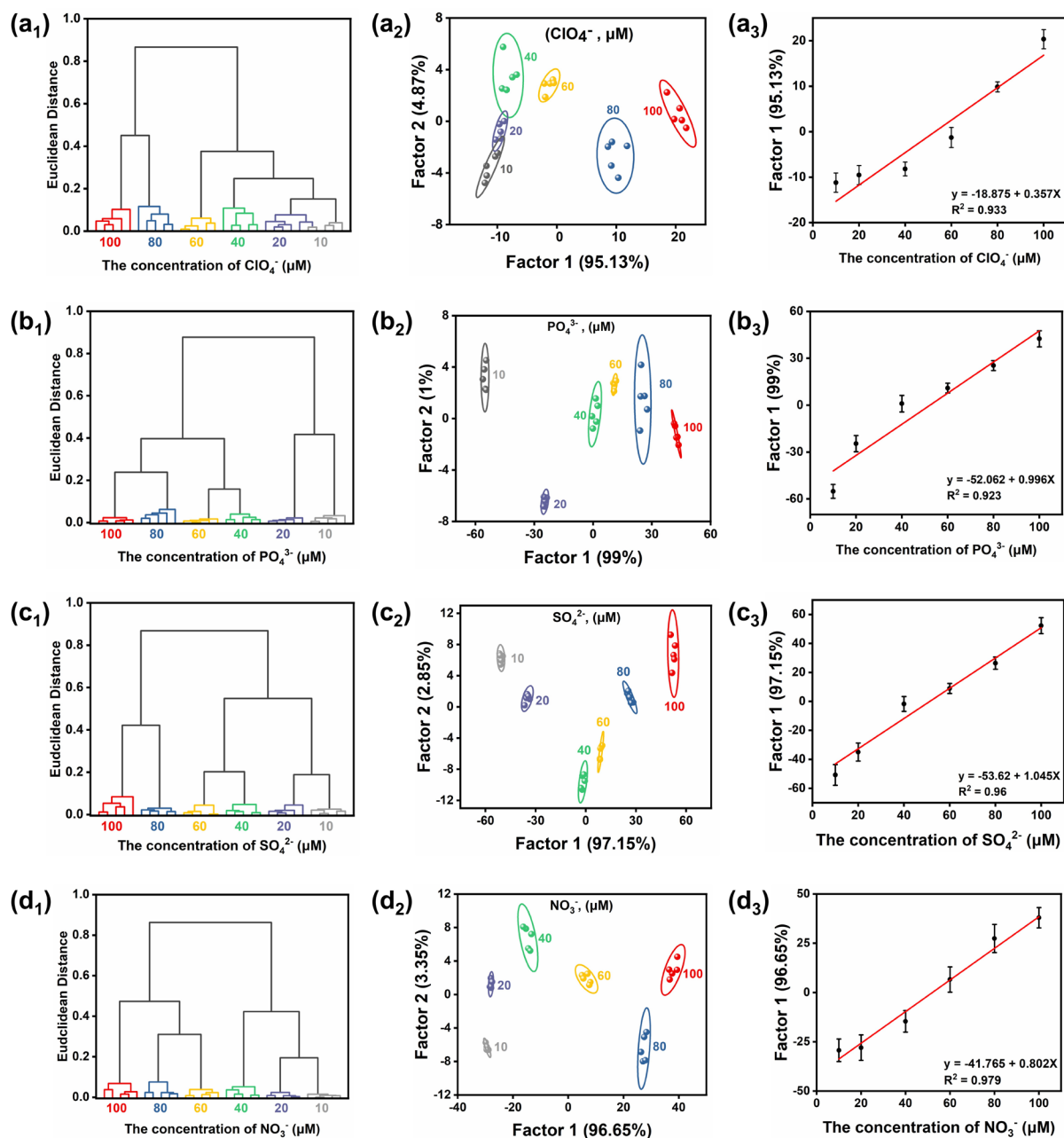
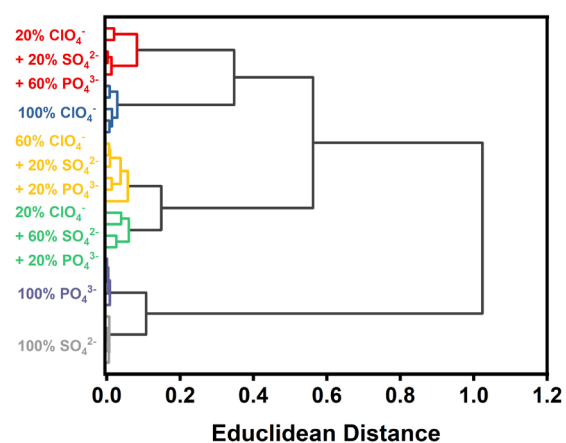
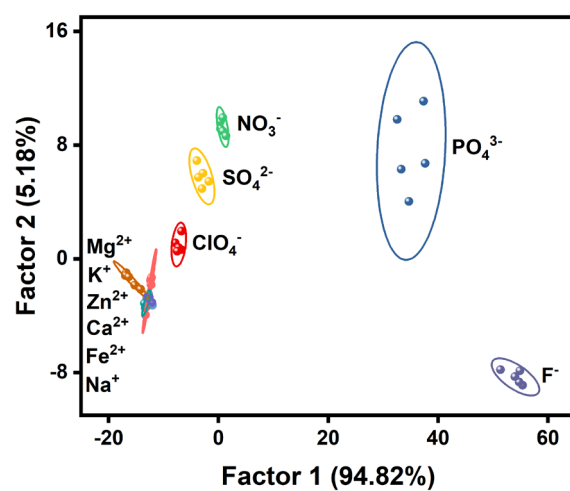


Fig. S7. (a₁) HCA and (a₂) LDA plot for fluorescence response patterns toward different concentrations of ClO_4^- . (a₃) Linear relationships between PC1 and various concentrations of ClO_4^- . (b₁) HCA and (b₂) LDA plot for fluorescence response patterns toward different concentrations of PO_4^{3-} . (b₃) Linear relationships between PC1 and various concentrations of PO_4^{3-} . (c₁) HCA and (c₂) LDA plot for fluorescence response patterns toward different concentrations of SO_4^{2-} . (c₃) Linear relationships between PC1 and various concentrations of SO_4^{2-} . (d₁) HCA and (d₂) LDA plot for fluorescence response patterns toward different concentrations of NO_3^- . (d₃) Linear relationships between PC1 and various concentrations of NO_3^- .



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 121 **Fig. S8.** HCA plot for fluorescence response patterns toward the mixtures of ClO_4^- , SO_4^{2-} , and
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124 **Fig. S9.** Anti-interference ability of the fluorescence sensor arrays.

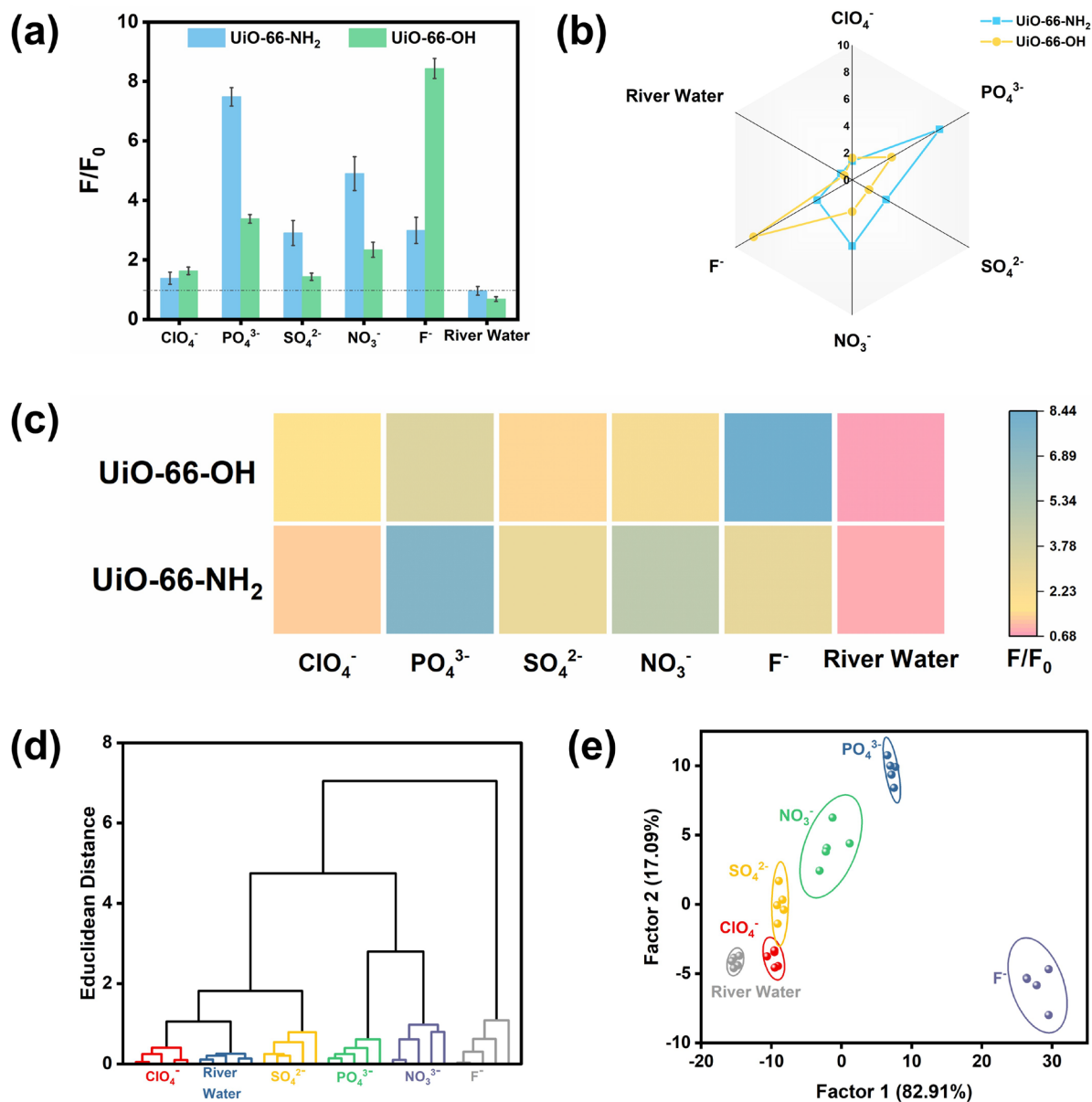


Fig. S10. (a) Fluorescent intensity ratio (F/F_0) responses and (b) Radar plot of UiO-66-NH₂ and UiO-66-OH to five anions (F^- , PO_4^{3-} , ClO_4^- , NO_3^- , and SO_4^{2-}) in river water. (c) Two-dimensional heat map generated from fluorescence patterns of fluorescence sensor array for the detection of five anions in river water. (d) HCA and (e) LDA plot for the identification of five anions derived from the fluorescence-response patterns.

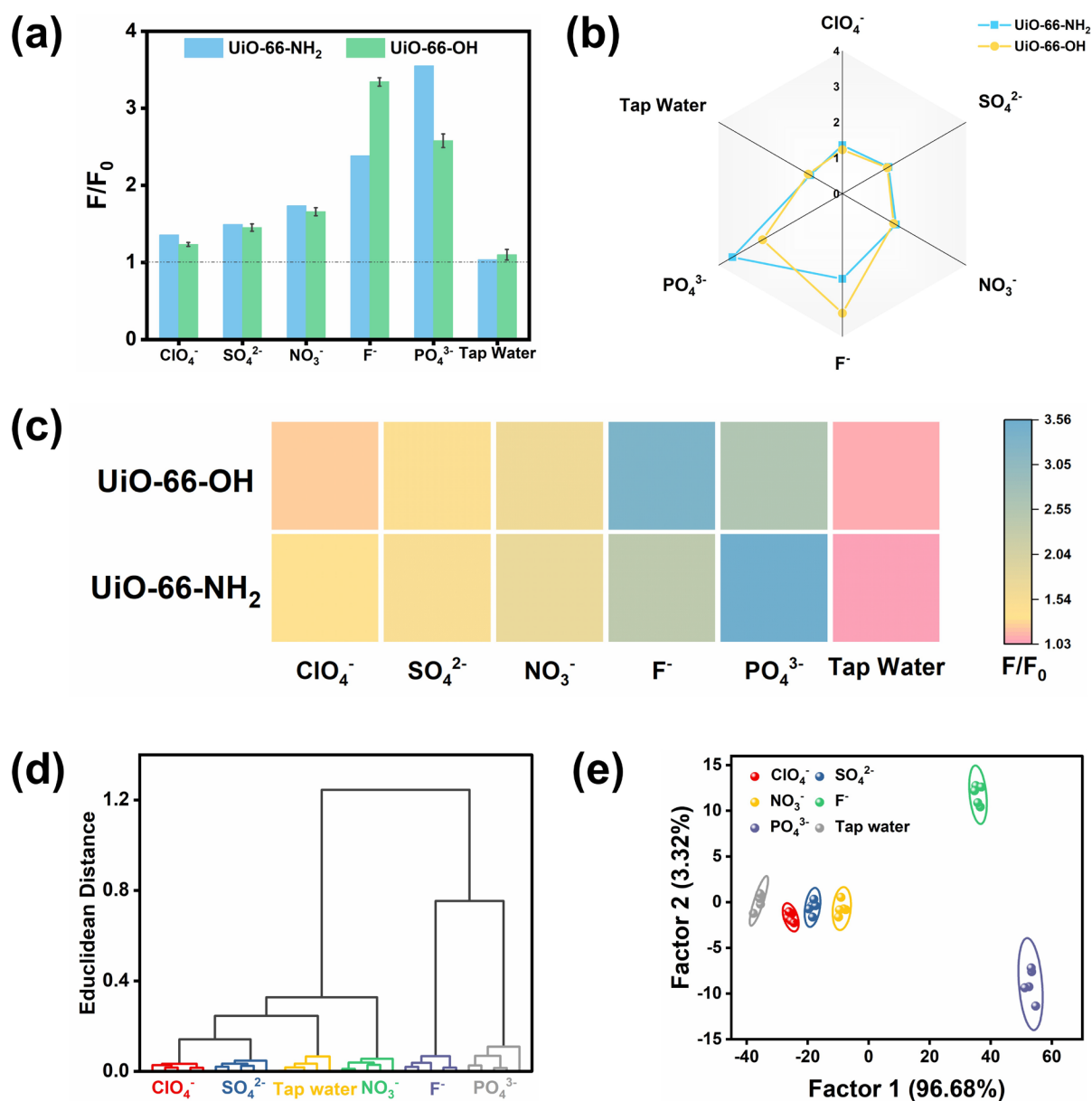


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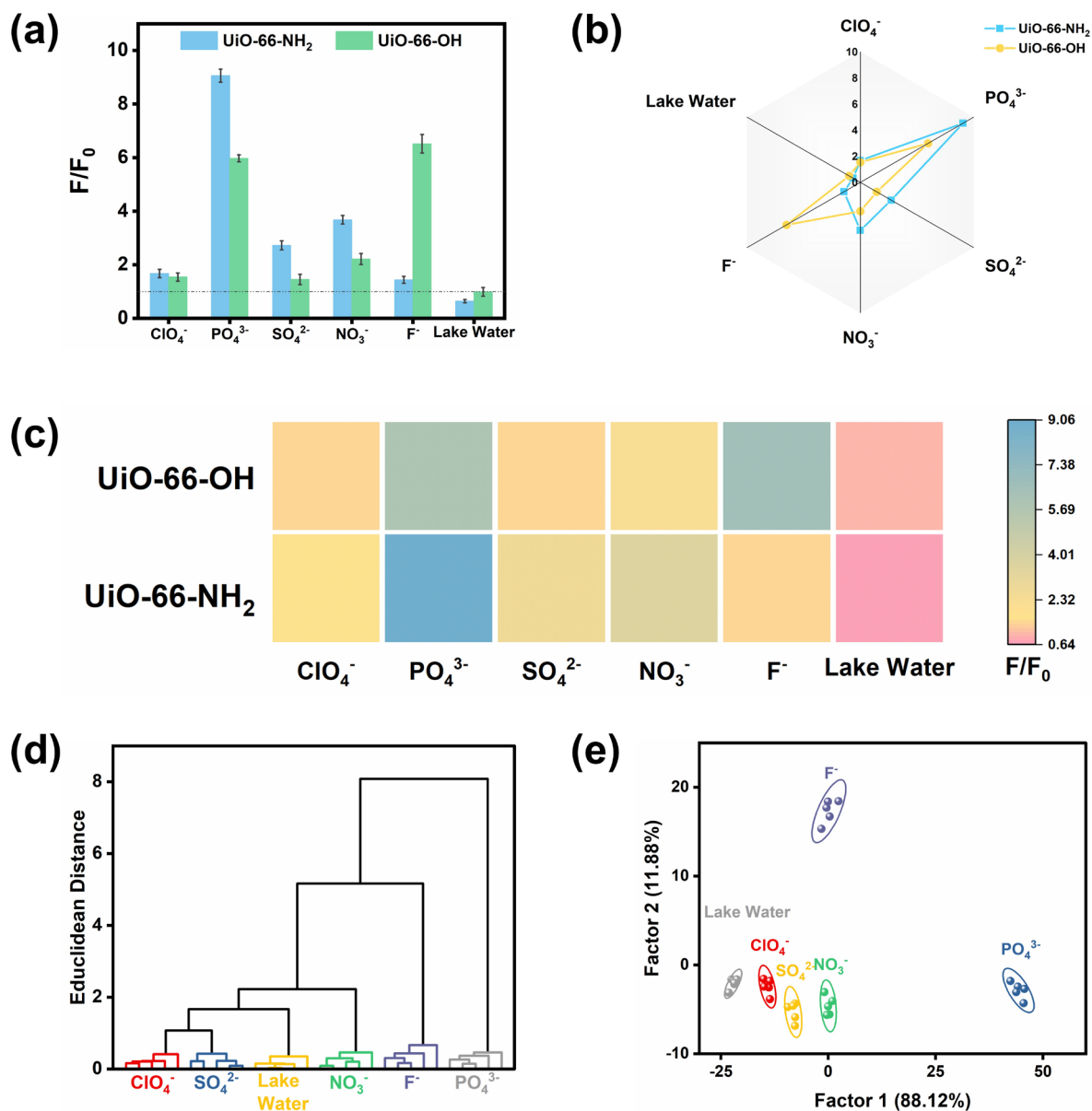


Fig. S12. (a) Fluorescent intensity ratio (F/F_0) responses and (b) Radar plot of UiO-66-NH₂ and UiO-66-OH to five anions (F⁻, PO₄³⁻, ClO₄⁻, NO₃⁻, and SO₄²⁻) in lake water. (c) Two-dimensional heat map generated from fluorescence patterns of fluorescence sensor array for the detection of five anions in lake water. (d) HCA and (e) LDA plot for the identification of five anions derived from the fluorescence-response patterns.

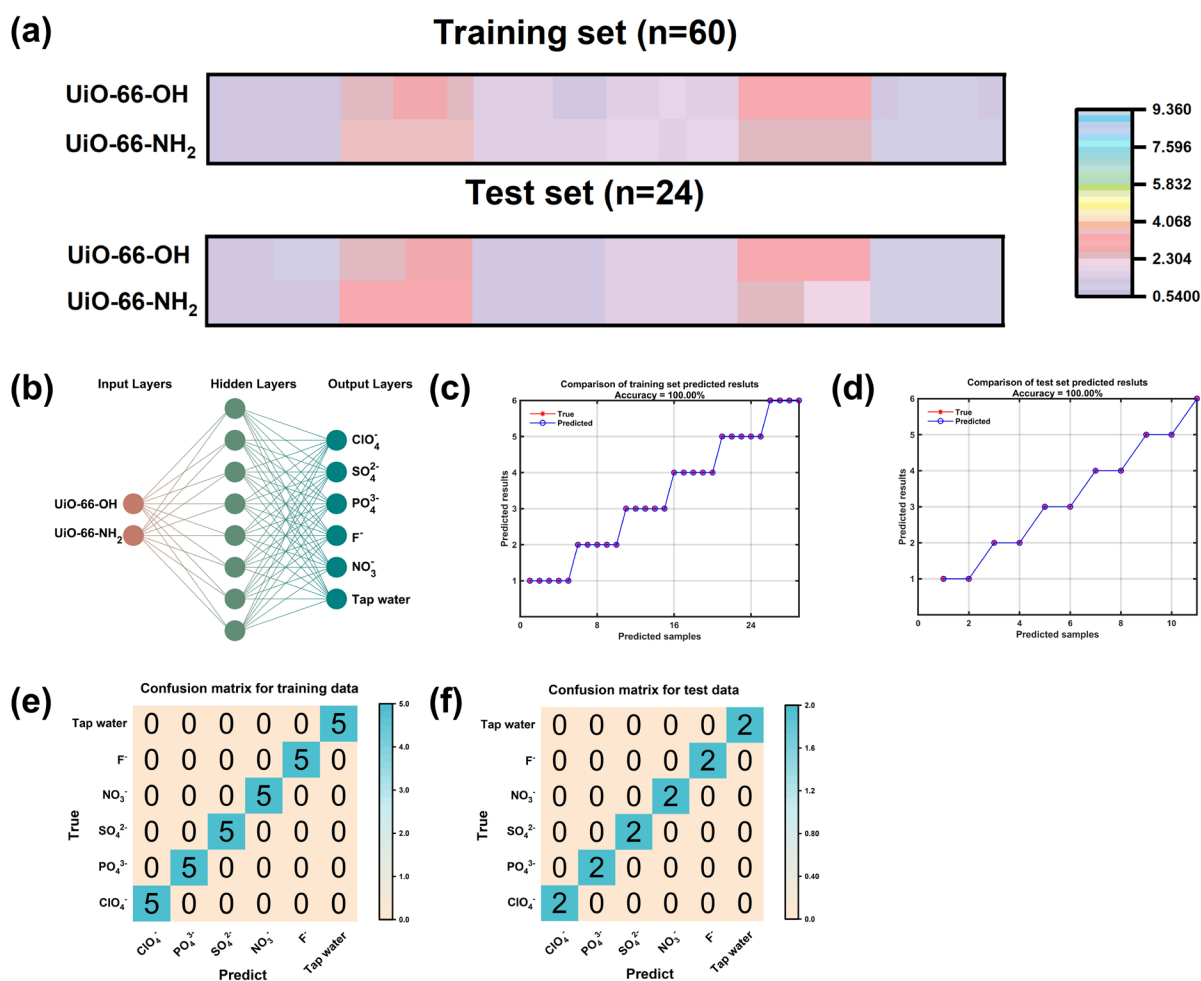


Fig. S13. Machine learning-supported fluorescent sensor array for the identification of five anions in tap water samples. (a) Heatmaps of randomly divided training sets (n=60) and test sets (n=24). (b) Schematic of ANN algorithm for five anions in tap water samples. Comparison of (c) training set predicted results and (d) test set predicted results. Confusion matrix for (e) training data and (f) test data.

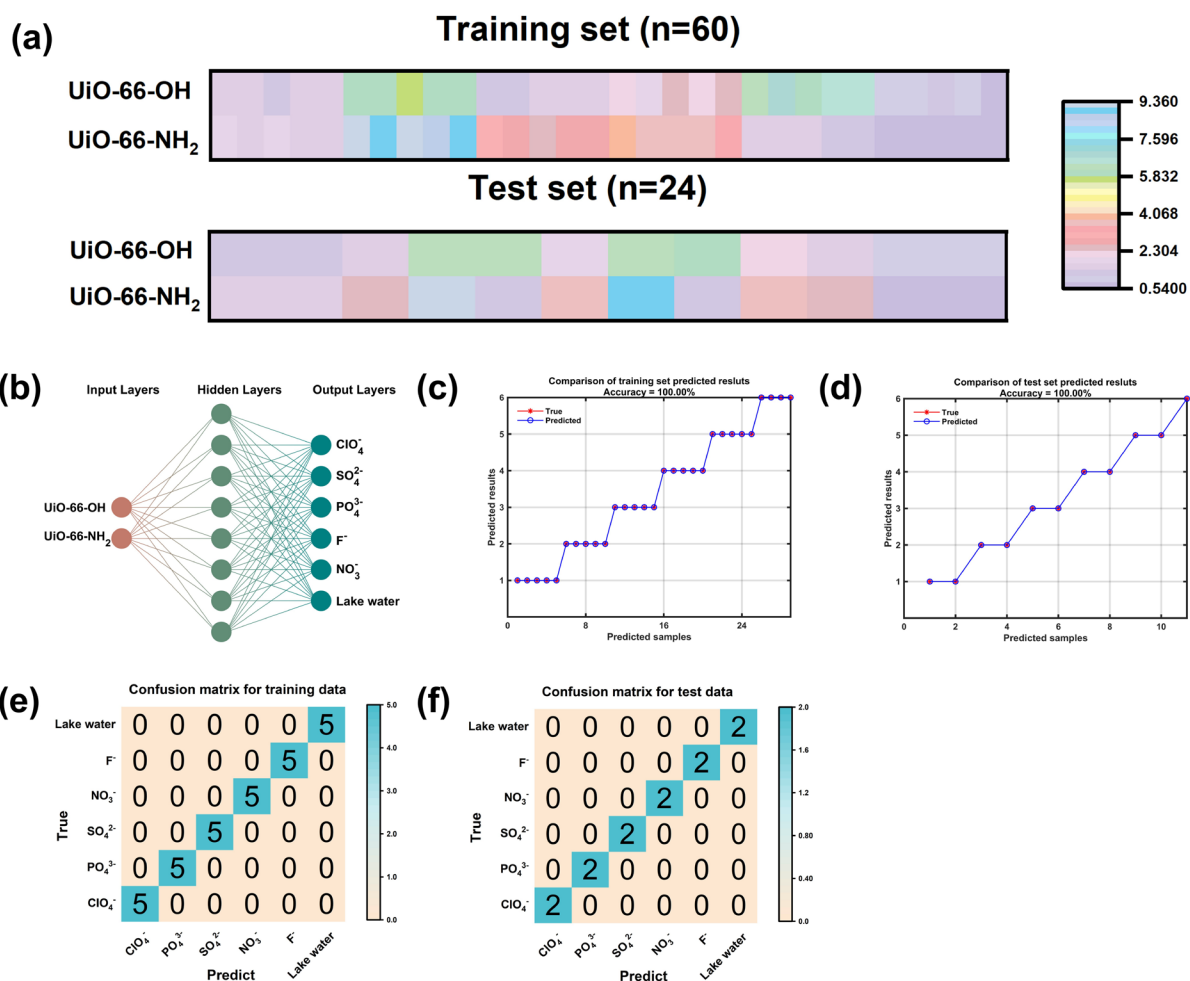


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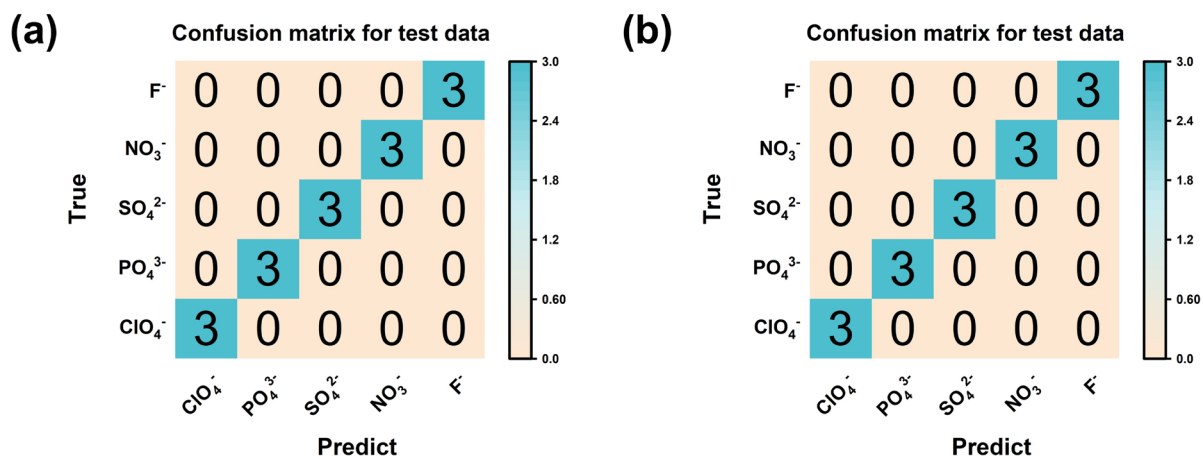


Fig. S15. Corresponding confusion matrix for five anions in blind (a) tap water and (b) lake water samples.

158 **Table S1.** Elemental quantification by XPS for UiO-66-NH₂ and UiO-66-OH.

LMOFs	Elements	Contents (%)
UiO-66-NH ₂	C	60.60
	O	20.83
	Zr	6.13
	N	10.47
UiO-66-OH	C	37.45
	O	44.41
	Zr	16.75
	N	1.38

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Table S2. Fluorescence lifetime of UiO-66-NH₂, UiO-66-OH, and UiO-66-NH₂ in the presence of F⁻.

Samples	Fluorescence lifetime
UiO-66-NH ₂	15.74
UiO-66-OH	3.24
UiO-66-NH ₂ +F ⁻	15.35

163 **Table S3.** Fluorescence sensor array for the quantitative detection of five anions.

Anions	Equations	Range (μM)	LOD (μM)	R^2
ClO_4^-	$y = -18.875 + 0.357x$	10-100	3.21	0.933
F^-	$y = -59.67 + 1.188x$	10-100	2.31	0.964
NO_3^-	$y = -41.765 + 0.802x$	10-100	3.15	0.979
PO_4^{3-}	$y = -52.062 + 0.996x$	10-100	2.14	0.923
SO_4^{2-}	$y = -53.62 + 1.045x$	10-100	3.51	0.96

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165 **Table S4.** Identification of blind samples with five anions spiked in river water.

Sample	UiO-66-NH ₂ (F/F ₀)	UiO-66-OH (F/F ₀)	Identification	Verification
1	1.6082	1.5941	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
2	3.0175	8.1585	F ⁻	F ⁻
3	2.6880	1.5385	SO ₄ ²⁻	SO ₄ ²⁻
4	3.4575	8.5515	F ⁻	F ⁻
5	7.7740	3.1221	PO ₄ ³⁻	PO ₄ ³⁻
6	2.8786	8.5435	F ⁻	F ⁻
7	1.2202	1.6845	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
8	4.6810	2.2875	NO ₃ ³⁻	NO ₃ ³⁻
9	3.4510	1.2375	SO ₄ ²⁻	SO ₄ ²⁻
10	7.2549	3.3844	PO ₄ ³⁻	PO ₄ ³⁻
11	2.2514	1.4902	SO ₄ ²⁻	SO ₄ ²⁻
12	4.7517	2.1468	NO ₃ ³⁻	NO ₃ ³⁻
13	1.1491	1.5944	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
14	4.1760	2.2456	NO ₃ ³⁻	NO ₃ ³⁻
15	6.9217	3.2350	PO ₄ ³⁻	PO ₄ ³⁻

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Table S5. Identification of blind samples with five anions spiked in tap water.

Sample	UiO-66-NH ₂ (F/F ₀)	UiO-66-OH (F/F ₀)	Identification	Verification
1	1.3714	1.2153	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
2	3.6815	2.4842	PO ₄ ³⁻	PO ₄ ³⁻
3	1.7714	1.6815	NO ₃ ³⁻	NO ₃ ³⁻
4	2.3315	3.3815	F ⁻	F ⁻
5	1.5114	1.4853	SO ₄ ²⁻	SO ₄ ²⁻
6	1.7514	1.6715	NO ₃ ³⁻	NO ₃ ³⁻
7	2.3815	3.4135	F ⁻	F ⁻
8	3.5135	2.6615	PO ₄ ³⁻	PO ₄ ³⁻
9	2.4515	3.2849	F ⁻	F ⁻
10	3.5515	2.5515	PO ₄ ³⁻	PO ₄ ³⁻
11	1.3681	1.2284	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
12	1.2981	1.1865	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
13	1.4384	1.4315	SO ₄ ²⁻	SO ₄ ²⁻
14	1.4735	1.4156	SO ₄ ²⁻	SO ₄ ²⁻
15	1.7151	1.5942	NO ₃ ³⁻	NO ₃ ³⁻

Table S6. Identification of blind samples with five anions spiked in lake water.

Sample	UiO-66-NH ₂ (F/F ₀)	UiO-66-OH (F/F ₀)	Identification	Verification
1	1.7816	1.3515	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
2	1.3870	1.5915	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
3	1.6715	1.6452	ClO ₄ ⁴⁻	ClO ₄ ⁴⁻
4	9.3361	5.8882	PO ₄ ³⁻	PO ₄ ³⁻
5	8.6715	6.0424	PO ₄ ³⁻	PO ₄ ³⁻
6	1.2945	6.6931	F ⁻	F ⁻
7	2.8539	1.1357	SO ₄ ²⁻	SO ₄ ²⁻
8	1.5776	6.8901	F ⁻	F ⁻
9	2.7843	1.3247	SO ₄ ²⁻	SO ₄ ²⁻
10	3.6915	2.4012	NO ₃ ³⁻	NO ₃ ³⁻
11	9.0415	5.7450	PO ₄ ³⁻	PO ₄ ³⁻
12	2.4804	1.5015	SO ₄ ²⁻	SO ₄ ²⁻
13	3.6442	2.2019	NO ₃ ³⁻	NO ₃ ³⁻
14	1.4113	6.3541	F ⁻	F ⁻
15	3.4330	2.5154	NO ₃ ³⁻	NO ₃ ³⁻



DSPACE

<https://dspace.org/>

Machine learning-driven sensor array based on luminescent metal–organic frameworks for simultaneous discrimination of multiple anions

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