Supporting Information

A minimized fluorescent chemosensor array utilizing carboxylate-attached polythiophenes on a chip for metal ions detection

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Contents

1. Emission quantum yield and emission lifetime

Table S1 The emission quantum yield (Φ) and emission lifetime (τ) of **2** and its complexes

Sample in DMSO	Φ (%)	τ_1 (ns)	τ_2 (ns)
2	19.0	< 0.1	0.58
2 with Cu^{2+}	0.9	ND	ND

[**2**] = 10 μM/unit, [Cu^{2+}] = 2.0 μM, λ_{ex} = 365 nm.

2. Selected fluorescence titrations

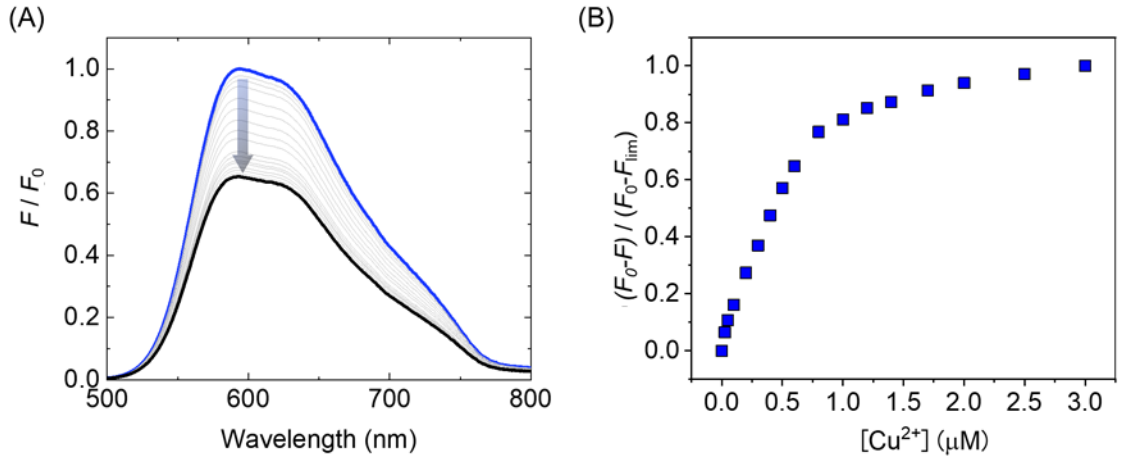

Fig. S1 (A) Fluorescence spectra of **1** in DMSO upon the addition of Cu^{2+} at 25 °C. (B) Fluorescence titration isotherm for Cu^{2+}. The titration isotherm was obtained by plotting the maximum emission at 594 nm. [Cu^{2+}] = 0 – 3.0 μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Cu^{2+}.

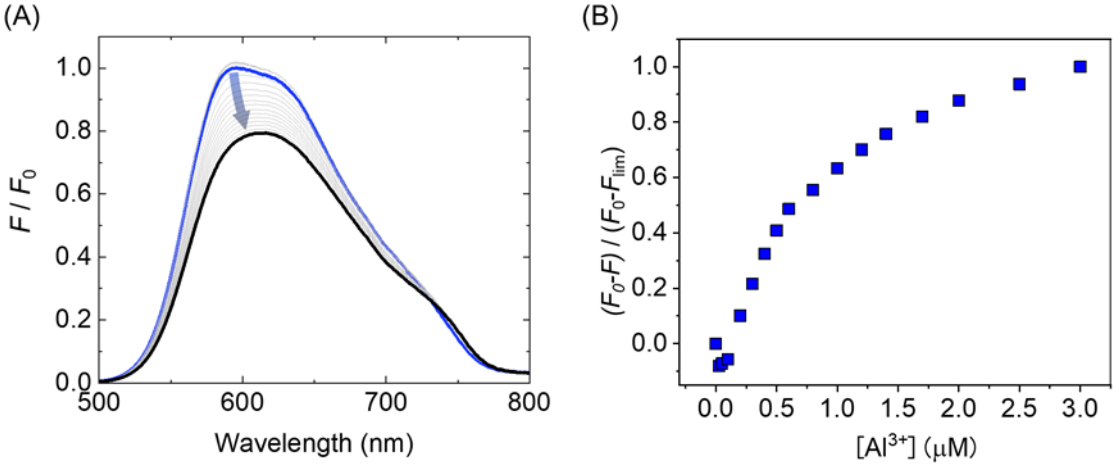

Fig. S2 (A) Fluorescence spectra of **1** in DMSO upon the addition of Al^{3+} at 25 °C. (B) Fluorescence titration isotherm for Al^{3+}. The titration isotherm was obtained by plotting the maximum emission at 594 nm. [Al^{3+}] = 0 – 3.0 μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Al^{3+}.

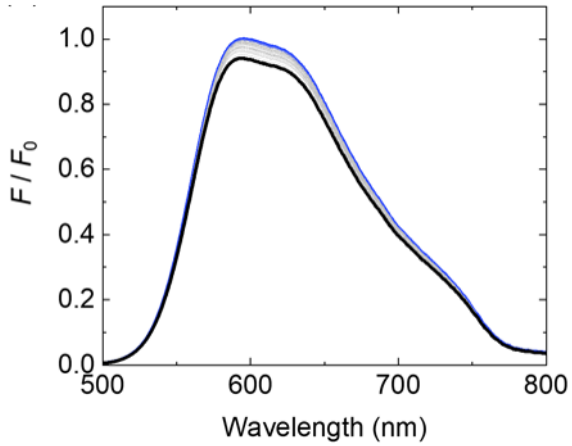

Fig. S3 Fluorescence spectra of **1** in DMSO upon the addition of Ca^{2+} at 25 °C. [Ca^{2+}] = 0 – 3.0 μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Ca^{2+}.

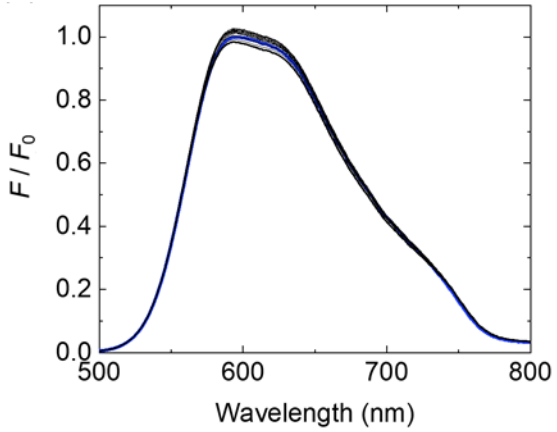

Fig. S4 Fluorescence spectra of **1** in DMSO upon the addition of Cd^{2+} at 25 °C. [Cd^{2+}] = 0 – 3.0 μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Cd^{2+}.

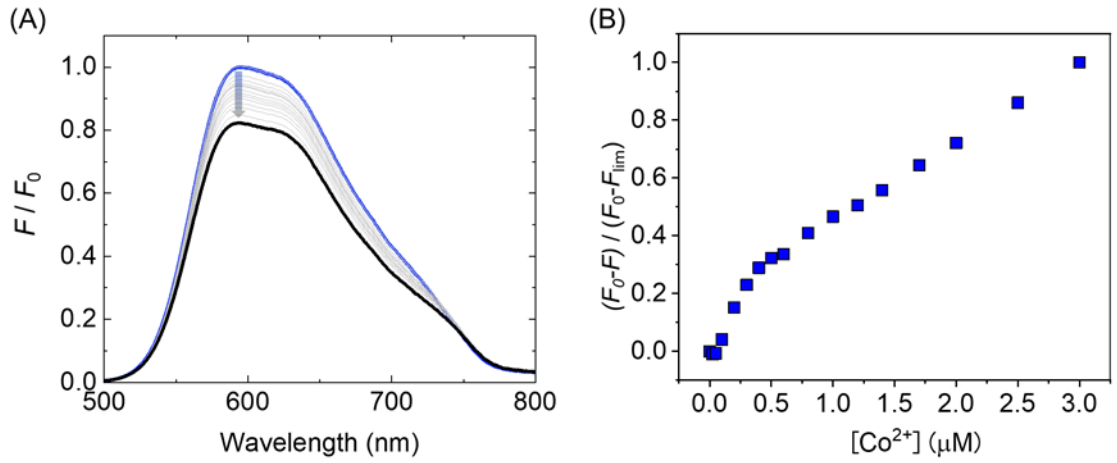

Fig. S5 (A) Fluorescence spectra of **1** in DMSO upon the addition of Co^{2+} at 25 °C. (B) Fluorescence titration isotherm for Co^{2+}. The titration isotherm was obtained by plotting the maximum emission at 594 nm. [Co^{2+}] = 0 – 3.0 μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Co^{2+}.

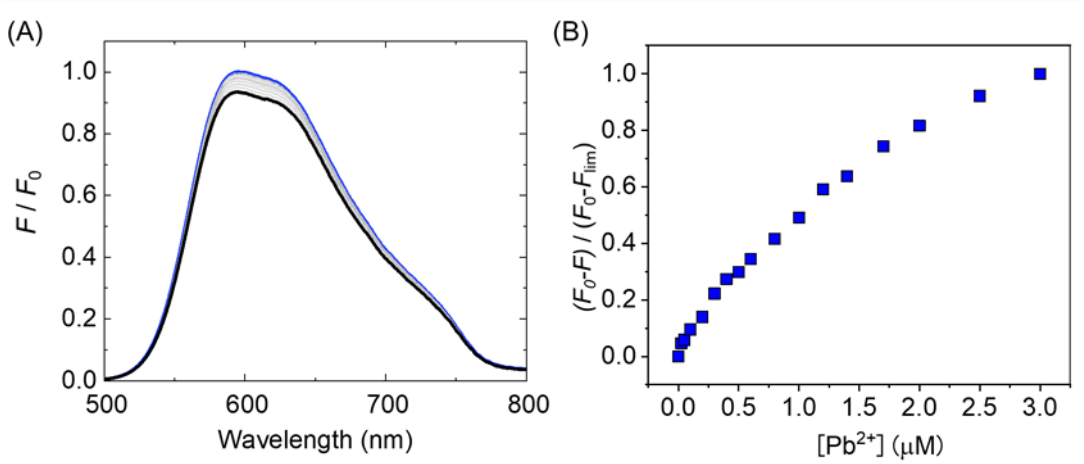

Fig. S6 (A) Fluorescence spectra of **1** in DMSO upon the addition of Pb^{2+} at 25 °C. (B) Fluorescence titration isotherm for Pb^{2+}. The titration isotherm was obtained by plotting the maximum emission at 594 nm. $[Pb^{2+}] = 0 – 3.0$ μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **1** and Pb^{2+}.

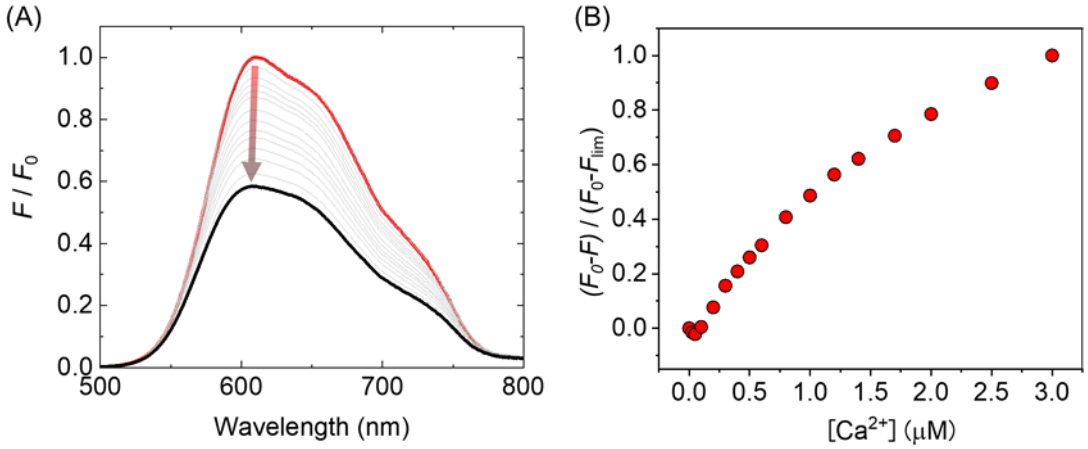

Fig. S7 (A) Fluorescence spectra of **2** in DMSO upon the addition of Ca^{2+} at 25 °C. (B) Fluorescence titration isotherm for Ca^{2+}. The titration isotherm was obtained by plotting the maximum emission at 610 nm. $[Ca^{2+}] = 0 – 3.0$ μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **2** and Ca^{2+}.

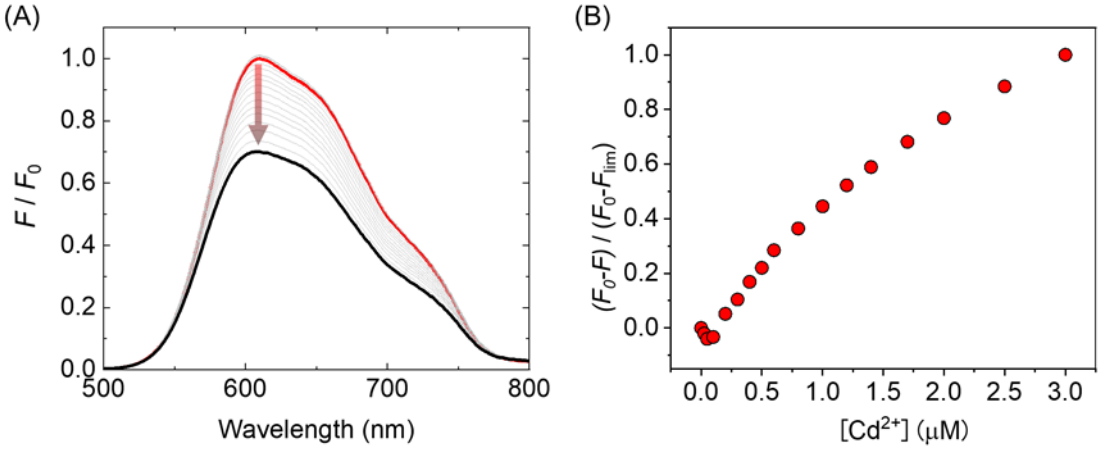

Fig. S8 (A) Fluorescence spectra of **2** in DMSO upon the addition of Cd^{2+} at 25 °C. (B) Fluorescence titration isotherm for Cd^{2+}. The titration isotherm was obtained by plotting the maximum emission at 610 nm. $[Cd^{2+}] = 0 – 3.0$ μM. λ_{ex} = 480 nm. The spectra were recorded in 10 min after mixing **2** and Cd^{2+}.

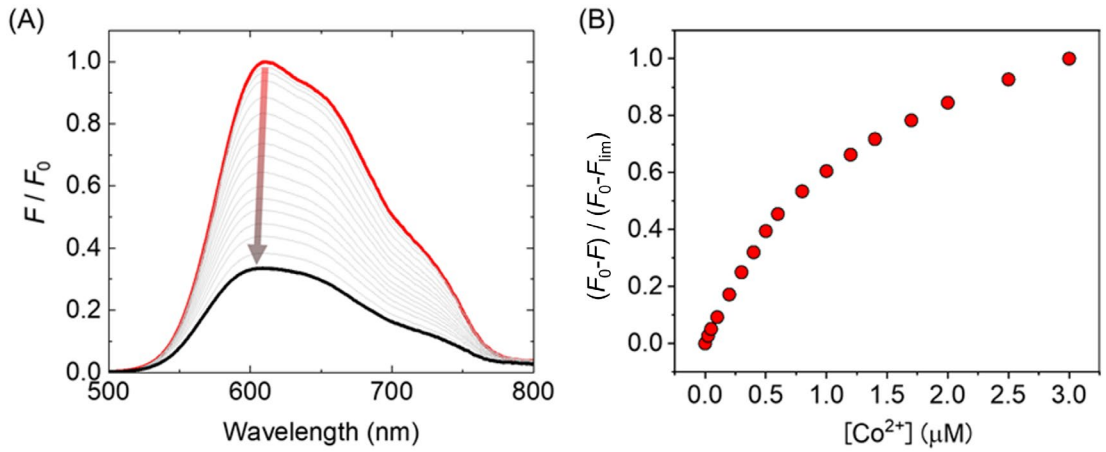

Fig. S9 (A) Fluorescence spectra of **2** in DMSO upon the addition of Co^{2+} at 25 °C. (B) Fluorescence titration isotherm for Co^{2+}. The titration isotherm was obtained by plotting the maximum emission at 610 nm. $[Co^{2+}] = 0 – 3.0$ μM. $\lambda_{ex} = 480$ nm. The spectra were recorded in 10 min after mixing **2** and Co^{2+}.

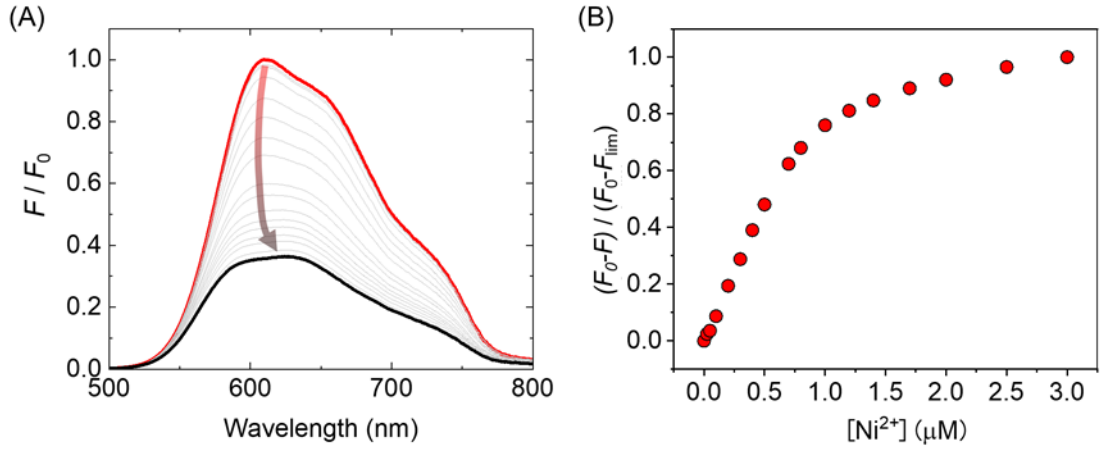

Fig. S10 (A) Fluorescence spectra of **2** in DMSO upon the addition of Ni^{2+} at 25 °C. (B) Fluorescence titration isotherm for Ni^{2+}. The titration isotherm was obtained by plotting the maximum emission at 610 nm. $[Ni^{2+}] = 0 – 3.0$ μM. $\lambda_{ex} = 480$ nm. The spectra were recorded in 10 min after mixing **2** and Ni^{2+}.

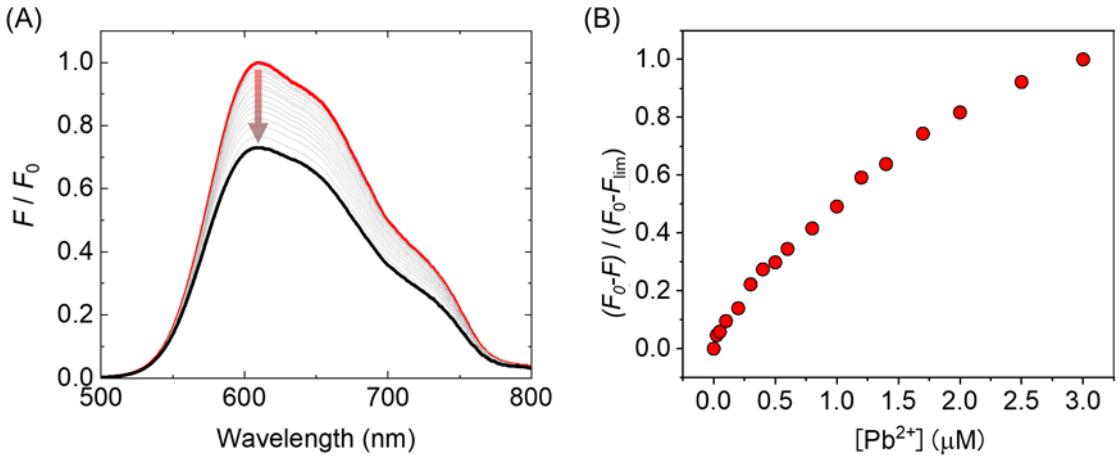

Fig. S11 (A) Fluorescence spectra of **2** in DMSO upon the addition of Pb^{2+} at 25 °C. (B) Fluorescence titration isotherm for Pb^{2+}. The titration isotherm was obtained by plotting the maximum emission at 610 nm. $[Pb^{2+}] = 0 – 3.0$ μM. $\lambda_{ex} = 480$ nm. The spectra were recorded in 10 min after mixing **2** and Pb^{2+}.

3. Limit of detection

Table S2 Limit of detection of the polymer sensors for metal ions

	P3CBT (ppb)	P3CPT (ppb)
Cu^{2+}	5.0	8.2
Al^{3+}	5.1	3.9
Ca^{2+}	13	22
Cd^{2+}	N.D.[a]	154
Co^{2+}	7.3	1.5
Ni^{2+}	2.5	2.3
Pb^{2+}	207	190
Zn^{2+}	6.2	1.5

[a] N.D.: not determined due to the small response.

4. Details of chemosensor array

Table S3 Datasets for the fluorescence image analysis

Light source	λ_{ex} (375 nm)	λ_{ex} (470 nm)	λ_{ex} (530 nm)
Long path (LP) and band path (BP) color filters for CCD camera	λ_{em} (450 nm BP 80[a])		
	λ_{em} (530 nm LP)	λ_{em} (530 nm LP)	
	λ_{em} (540 nm BP 100[b])		
	λ_{em} (580 nm LP)	λ_{em} (580 nm LP)	λ_{em} (580 nm LP)
	λ_{em} (630 nm LP)	λ_{em} (630 nm LP)	λ_{em} (630 nm LP)
		λ_{em} (700 nm BP 70[c])	λ_{em} (700 nm BP 70[c])

The wavelength ranges for the band path filters; [a]410−490 nm, [b]490−590 nm, and [c]665−735 nm, respectively.

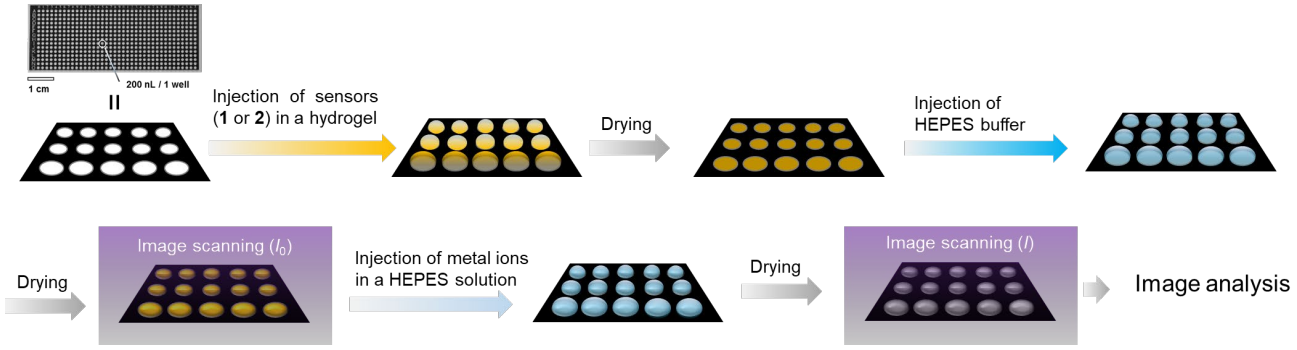

Fig. S12 Schematic illustration of the fabrication process for the microarray chip.

Table S3 Jackknifed classification matrix for linear discriminant analysis

	Cu^{2+}	Al^{3+}	Ca^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	control	%correct
Cu^{2+}	28	0	0	0	0	0	0	0	0	100
Al^{3+}	0	28	0	0	0	0	0	0	0	100
Ca^{2+}	0	0	28	0	0	0	0	0	0	100
Cd^{2+}	0	0	0	28	0	0	0	0	0	100
Co^{2+}	0	0	0	0	28	0	0	0	0	100
Ni^{2+}	0	0	0	0	0	28	0	0	0	100

Pb^{2+}	0	0	0	0	0	0	28	0	0	100
Zn^{2+}	0	0	0	0	0	0	0	28	0	100
control	0	0	0	0	0	0	0	0	28	100
total	28	28	28	28	28	28	28	28	28	100

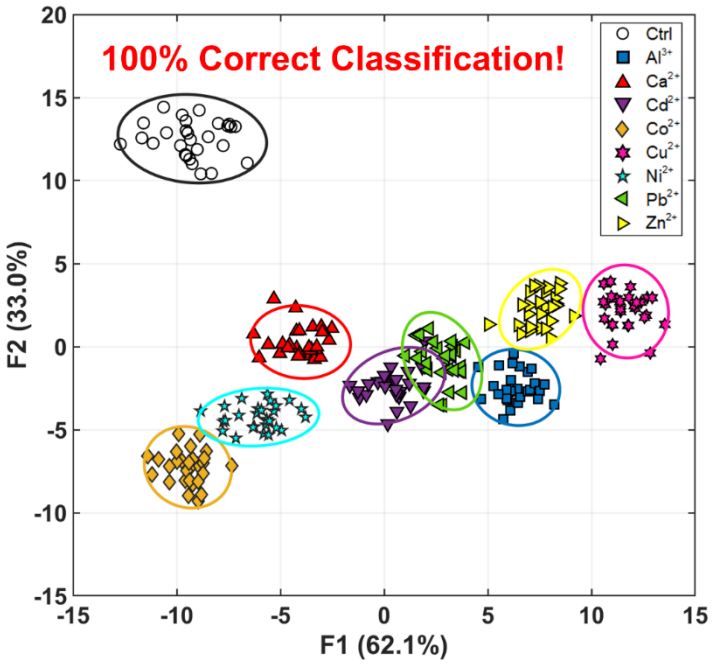

Fig. S13 LDA canonical score plot with 99% confidence ellipsoids for the qualitative analysis of the 8 types of the metal ions in a HEPES buffer (50 mM) with NaCl (10 mM) at pH 7.4. For each trial, 28 repetitions were conducted. [Hydrogel] = 3.6wt%, [**1**] = [**2**] = 250 μM/unit. [Metal ion] = 10 μM.

Table S4 List of concentrations for the quantitative analysis in the mixture. The grey line indicates the validation datasets and the white lines indicate the calibration datasets. All solutions were prepared in HEPES buffer (50 mM) with NaCl (10 mM) at pH 7.4.

Cu^{2+} (ppm)	0	1.28	1.92	3.2	3.84	5.12
Al^{3+} (ppm)	2.16	1.62	1.35	0.81	0.54	0