Electronic Supplementary Material

A sensor array based on DNA-wrapped bimetallic zeolitic imidazolate frameworks for detection of ATP hydrolysis products

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Chemicals. Zinc nitrate ($Zn(NO_3)_2$), manganese chloride ($MnCl_2$), copper chloride ($CuCl_2$), nickel chloride ($NiCl_2$), 2-methylimidazole (2-MI), sodium pyrophosphate (PPi), adenosine monophosphate (AMP), guanosine monophosphate (GMP), cytidine monophosphate (CMP), adenosine diphosphate (ADP), adenosine triphosphate (ATP), guanosine triphosphate (GTP), cytidine triphosphate (CTP), sodium triphosphate (STPP), bovine serum albumin (BSA) and fetal bovine serum (FBS) were purchased from Sigma-Aldrich. 4-(2-hydroxyethyl) piperazine-1-ethane sulfonate (HEPES) and the four nucleosides were obtained from Mandel Scientific (Guelph, Ontario, Canada). Milli-Q water was used to prepare buffers and solutions. The DNA samples were purchased from Integrated DNA Technologies (IDT, Coralville, IA, USA):

FAM-12mer: 5′-FAM-AGAGAACCTGGG-3′

Random DNA (rDNA): 5′-TCACAGATGCGT-3′

Apparatus and Characterization. Zeta-potential was measured using dynamic light scattering (DLS, Zetasizer Nano 90, Malvern). The morphologies and structural analysis of different ZIFs were carried out by transmission electron microscopy (TEM, Phillips CM10 100 kV microscope) and powder X-ray diffraction (PXRD, Bruker D8). Fourier transform infrared (FT-IR) spectra were recorded with a Tensor 27 spectrometer (Bruker Optics, Ettlingen, Germany) using KBr pellets in the range of 4000-400 cm^{-1}. The amount of the actual metal ions in M/Zn-ZIF (M=Ni, Mn, Cu) was measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900). The fluorescent intensity was recorded on a microplate reader (Infinite F200 Pro, Tecan) with excitation at 485 nm and emission at 535 nm.

Table S1 The molarity, and the theoretical and actual metal ions doping percentages in each sample by ICP-OES analysis.

Sample	**2-MI (mmol)**	**$Zn(NO_3)_2$ (mmol)**	**M^{2+}(Cu^{2+}, Mn^{2+}, Ni^{2+}) (mmol)**	**Theoretical M^{2+} doping percentage (%)**	**Actual M^{2+} percentage (%)**
ZIF-8	4	0.5	0	0	0
Cu/ZIF-8	4	0.4	0.1	20	5.09
Mn/ZIF-8	4	0.4	0.1	20	1.14
Ni/ZIF-8	4	0.4	0.1	20	0.46

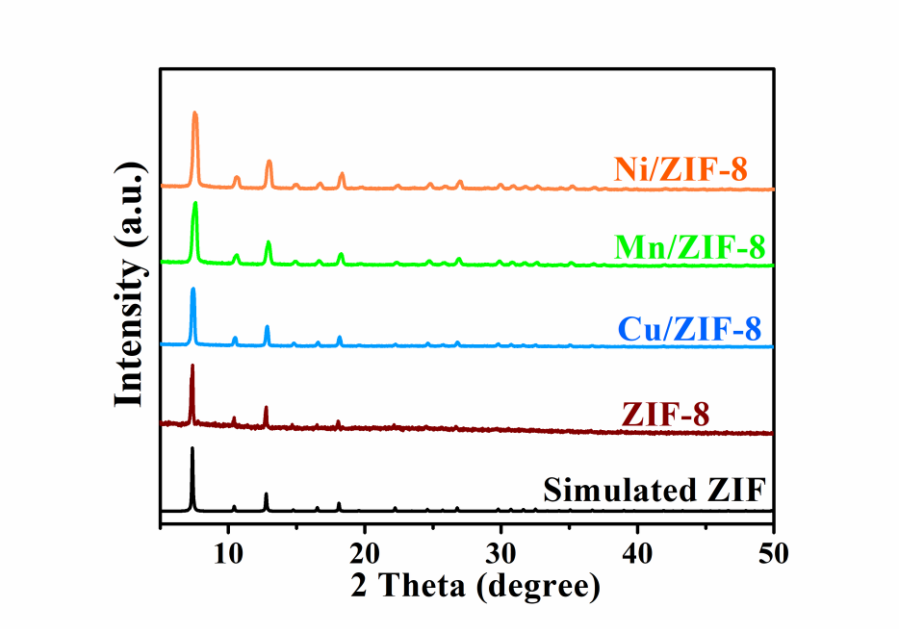

Figure S1. PXRD patterns of ZIF-8, Cu/ZIF-8, Mn/ZIF-8 and Ni/ZIF-8.

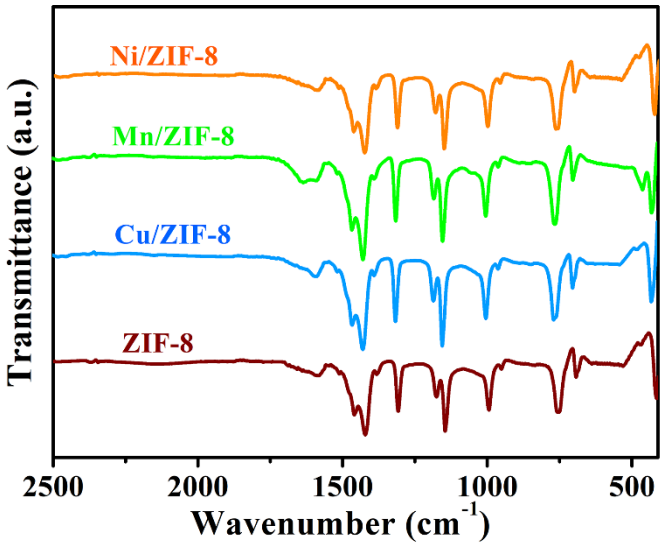

Figure S2. FT-IR spectra of ZIF-8, Cu/ZIF-8, Mn/ZIF-8 and Ni/ZIF-8.

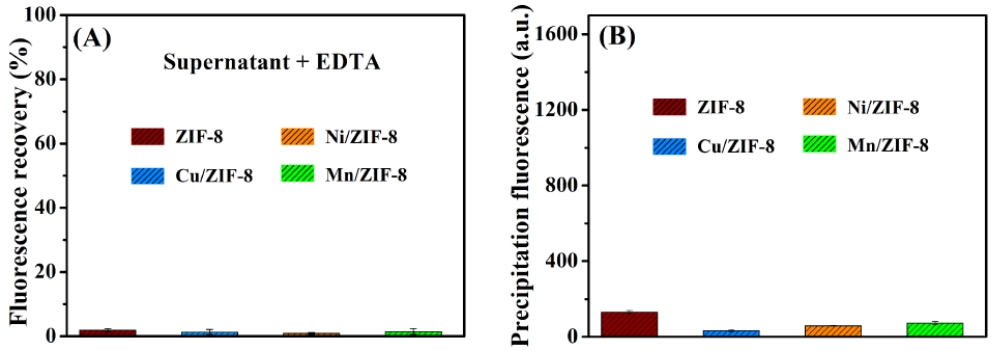

Figure S3. (A) Fluorescence recovery of the supernatants after the addition of 1 mM EDTA. This experiment indicated that very little DNA desorbed. (B) Re-dispersed precipitate fluorescence after FAM-12mer (10 nM) adsorbed on ZIFs. This experiment indicated that the adsorbed DNA strands were tightly adsorbed.

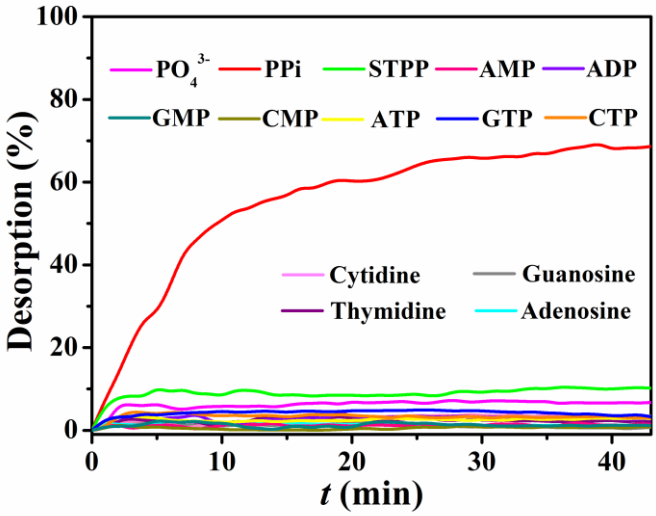

Figure S4. Desorption kinetics of FAM-12mer (10 nM) from Cu/ZIF-8 (200 μg/mL) induced by 1 mM different phosphate-containing species.

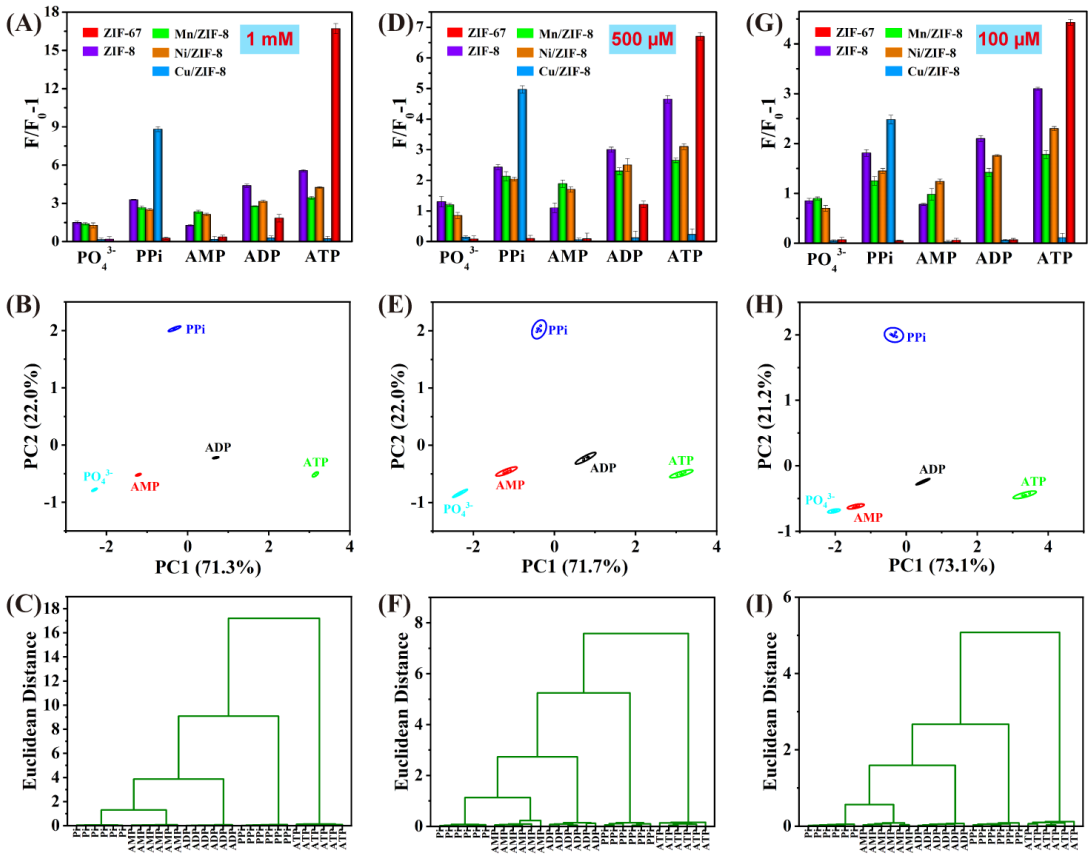

Figure S5. The relative fluorescence enhancement and corresponding principal component analysis (PCA) and hierarchical cluster analysis (HCA) plot of ZIF sensor arrays towards different concentrations of five phosphates: (A, B, C) 1 mM, (D, E, F) 500 μM, (G, H, I) 100 μM. Each error bar was calculated from six independent measurements, and the ellipses indicate 95% confidence.

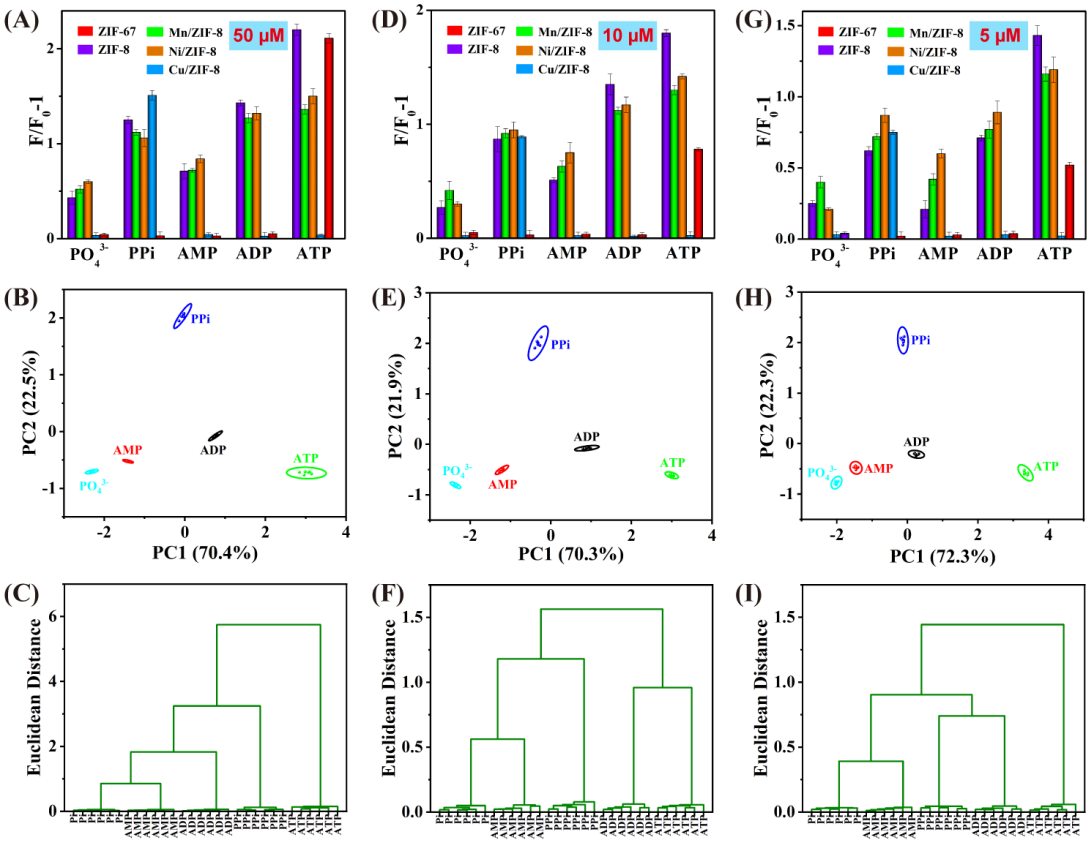

Figure S6. The relative fluorescence enhancement and corresponding principal component analysis (PCA) and hierarchical cluster analysis (HCA) plot of ZIF sensor arrays towards different concentrations of five phosphates: (A, B, C) 50 μM, (D, E, F) 10 μM, (G, H, I) 5 μM. Each error bar was calculated from six independent measurements, and the ellipses indicate 95% confidence.

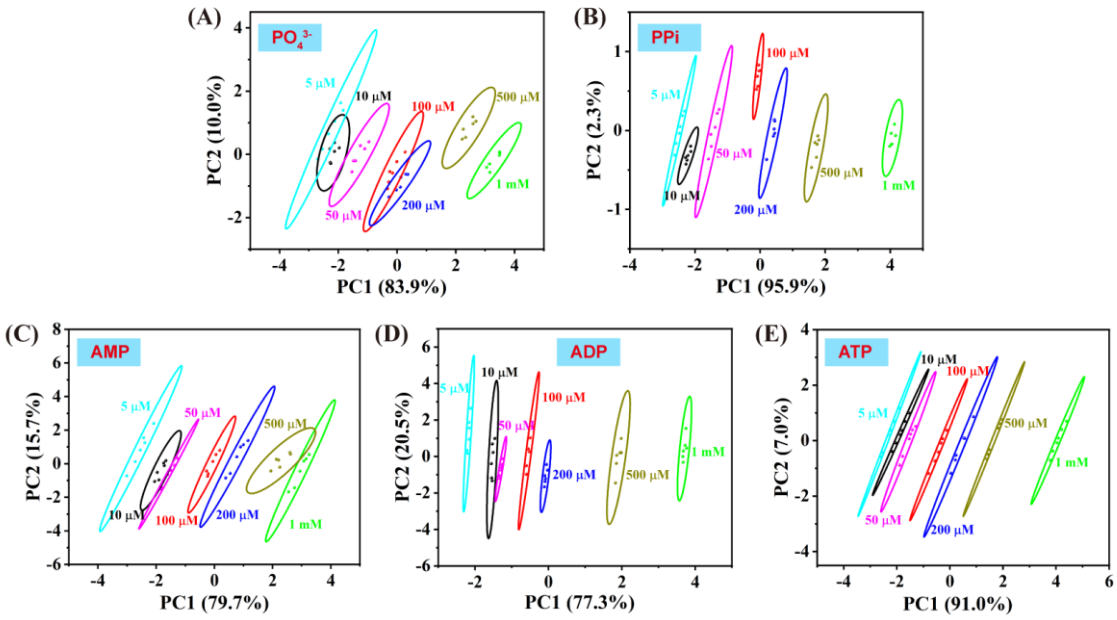

Figure S7. Principal component analysis (PCA) of the ZIF sensor array for the identification of different concentrations of (A) PO_4^{3-}, (B) PPi, (C) AMP, (D) ADP, and (E) ATP based on the relative fluorescence enhancement. Each measurement was repeated six times, and the ellipses indicate 95% confidence.