Supporting Information

Title: Nanopore Detection of Copper Ions using a Polyhistidine Probe

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Figure S1. Effect of the applied voltage bias on the (a) mean residence time and (b) frequency of the long-lived events due to Cu^{2+} -peptide complexes. The experiments were performed in a buffer solution comprising 1.0 M NaCl and 10 mM Tris•HCl (pH 7.5) in the presence of 40 μ M peptide H10 and 15 μ M Cu²⁺ ions.



Figure S2. Typical single-channel current recording traces of peptide H10 in the absence and presence of Cu²⁺ ions at (a) pH 6.5, (b) pH 7.5, and (c) pH 8.5, showing the effect of pH on nanopore detection of Cu²⁺. The experiments were performed with the (M113F)₇ α -hemolysin pore in a buffer solution comprising 1.0 M NaCl and 10 mM Tris•HCl at +100 mV (*cis* at ground) in the presence of 40 μ M H10.



Figure S3. Effects of the applied voltage bias and solution pH on the short-lived events due to free peptides. (a) Residence time plot; and (b) event frequency plot. The experiments were performed in a buffer solution comprising 1.0 M NaCl and 10 mM Tris•HCl in the presence of 40 μ M peptide H10.



Figure S4. Event signatures of peptide H10 in the presence of various metal ions, demonstrating that Cu²⁺-peptide complexes could be different from other metal ion-peptide complexes based on event residence times and/or blockage amplitudes. The experiments were performed with the (M113F)₇ α -hemolysin pore at +100 mV in the presence of 40 μ M H10 and 10 μ M metal ions.



Figure S5. Pie chart showing the contribution from various metal ion-peptide complexes to the current modulation events observed in the nanopore. The experiments were performed with the (M113F)₇ α -hemolysin pore at +100 mV in the presence of 40 μ M H10 and 10 μ M metal ions. Only the events having the residence times larger than 15 ms, and with residual currents within the range from 4 pA to 10 pA were included in the data analysis.



Figure S6. Event signatures of peptide H10 in the presence of Cu^{2+} ions. (a) Scatter plot of event residence time versus amplitude; (b) amplitude histogram; (c) residence time histogram of the short-lived events due to free peptides; and (d) residence time histogram of the long-lived events due to Cu^{2+} -peptide complexes. The experiments were performed with the (M113F)₇ α -hemolysin pore in a buffer solution comprising 1.0 M NaCl and 10 mM Tris+HCl (pH 7.5) at +160 mV (*cis* at ground). The concentrations of peptide H10 and Cu²⁺ ions were 40 μ M, and 200 nM, respectively.



Figure S7. Detection of Cu^{2+} ions using a wide-type α -hemolysin pore. (a) Typical trace segments; (b) scatter plots of event residence time versus amplitude; (c) amplitude histograms; and (d) residence time histograms (note that only the long-lived events were included in the data analysis at 5 μ M and 10 μ M concentrations of Cu^{2+} ions). The experiments were performed at +100 mV in the presence of 40 μ M H10.