

Electronic supplementary information (ESI)

**Metal-organic complex functionalized protein nanopore
sensor for aromatic amino acids chiral recognition**

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Supporting Figures and table

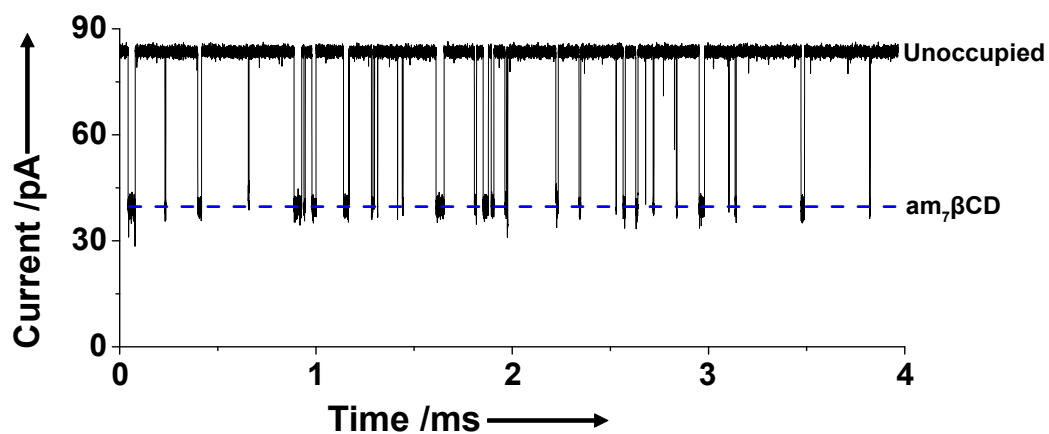


Fig. S1 Representative current traces showing no detectable current block in open and am₇βCD block current levels for a mixture of 20 nature L-α-amino acids (AAS) in (M113R)₇ nanopore. Condition: 40 μM am₇βCD added from the trans compartment and a mixture of AAS (20 μM of each L-α-amino acid) from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV. The same phenomena is for hepta-6-sulfato-βCD (S₇βCD) as an adapter.

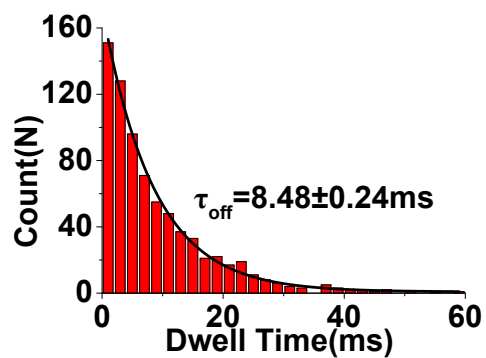
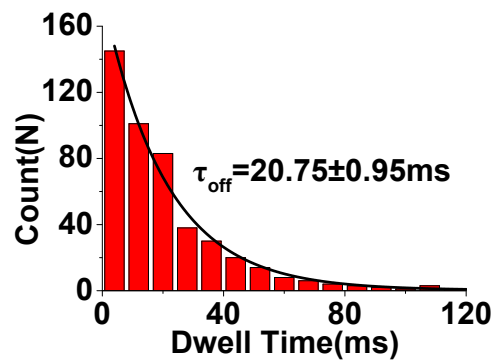
a**b**

Fig. S2 Dwell-time histograms with exponential fits for the events arising from (a) am₇βCD and (b) am₇βCD-Cu^{II}. Experiment condition: 1 M NaCl, 10 mM MOPS buffer, pH 8.0, +100mV, 40 μM am₇βCD and 20 μM CuCl₂ added from the trans compartment.

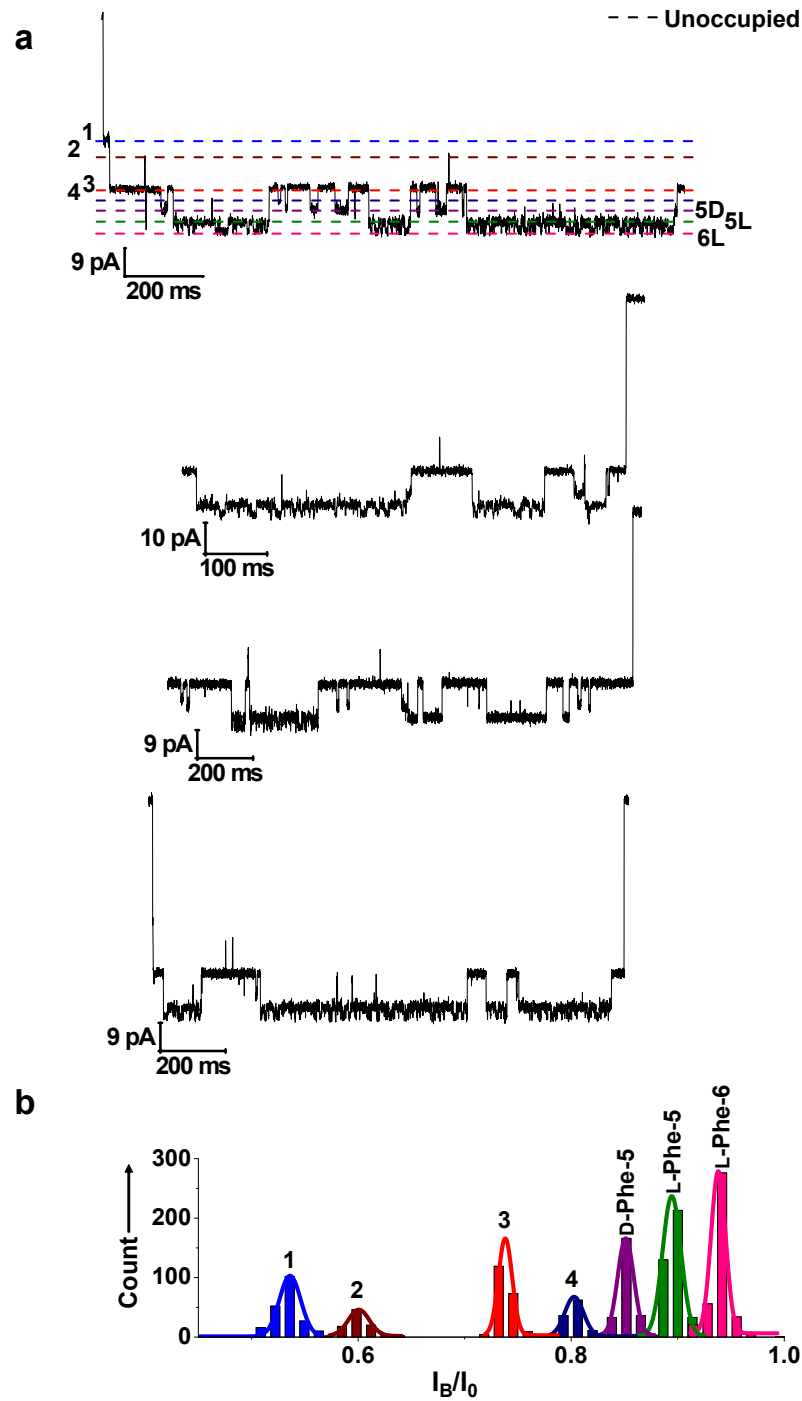


Fig. S3 Representative extensive current traces (a) from single (M113R)₇ pore at +100 mV showing the interaction of pore with mixture of L-Phe, D-Phe, am₇βCD and CuCl₂. (b) The corresponding blockage current event histograms. Experiment condition: 40 μM am₇βCD and 20 μM CuCl₂ added from the trans compartment and 20 μM L-Phe and 20 μM D-Phe from the cis side, 1 M NaCl, 10 mM MOPS buffer, pH 8.0.

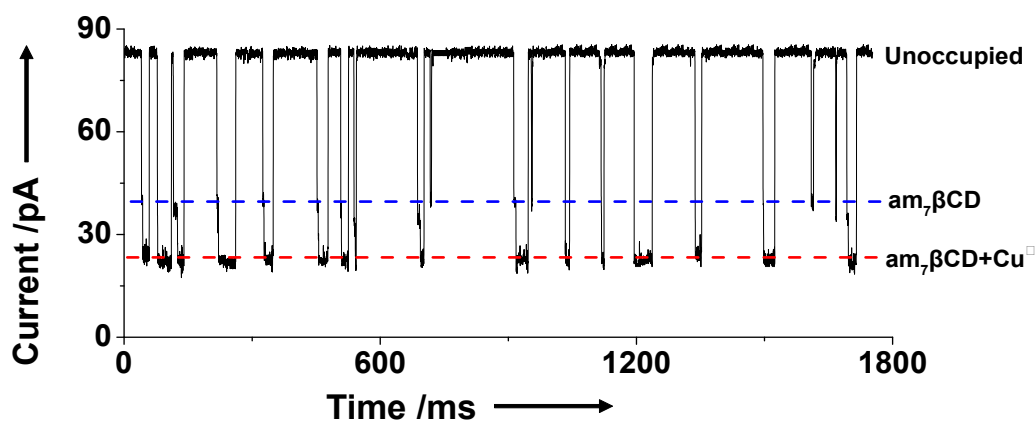


Fig. S4 Representative current traces showing a mixture of L-aliphatic α -amino acids no interaction with cyclodextrin metal complexes in nanopore. Condition: 40 μ M am₇βCD and 20 μ M CuCl₂ added from the trans compartment and L-aliphatic α -amino acids (20 μ M for each amino acid.) from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

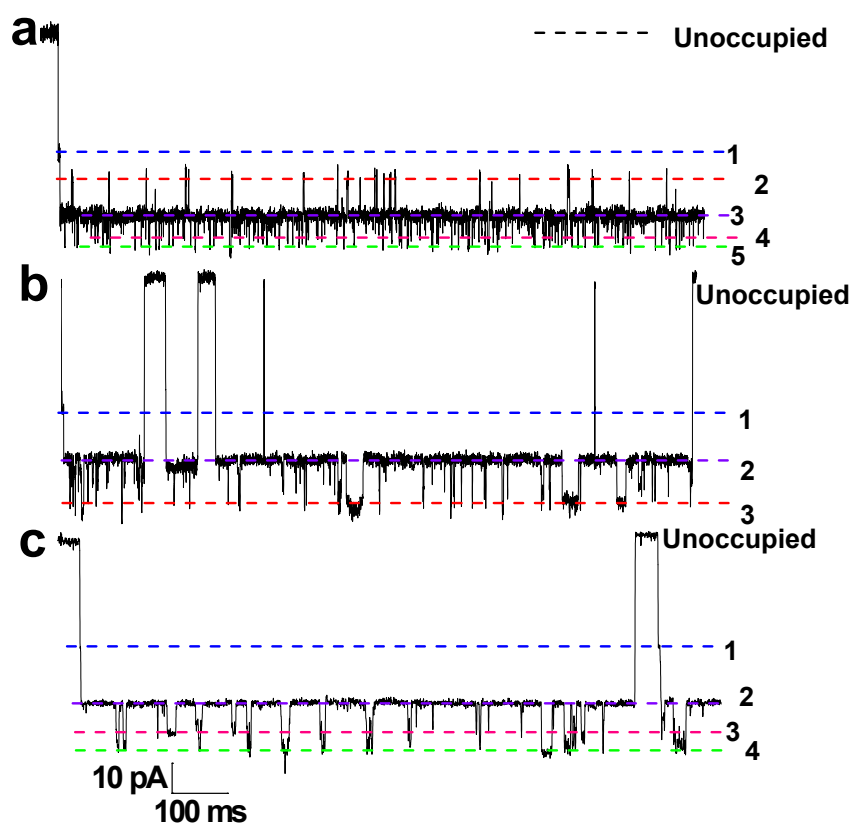


Fig. S5 Representative current traces showing (a) L-dopar (b) 5-sulfosalicylic acid and (c) L-mandelic acid interaction with cyclodextrin metal complexes in nanopore. Condition: 40 μM $\alpha\text{-CD}$ and 20 μM CuCl_2 added from the trans compartment and 20 μM for each aromatic compounds from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

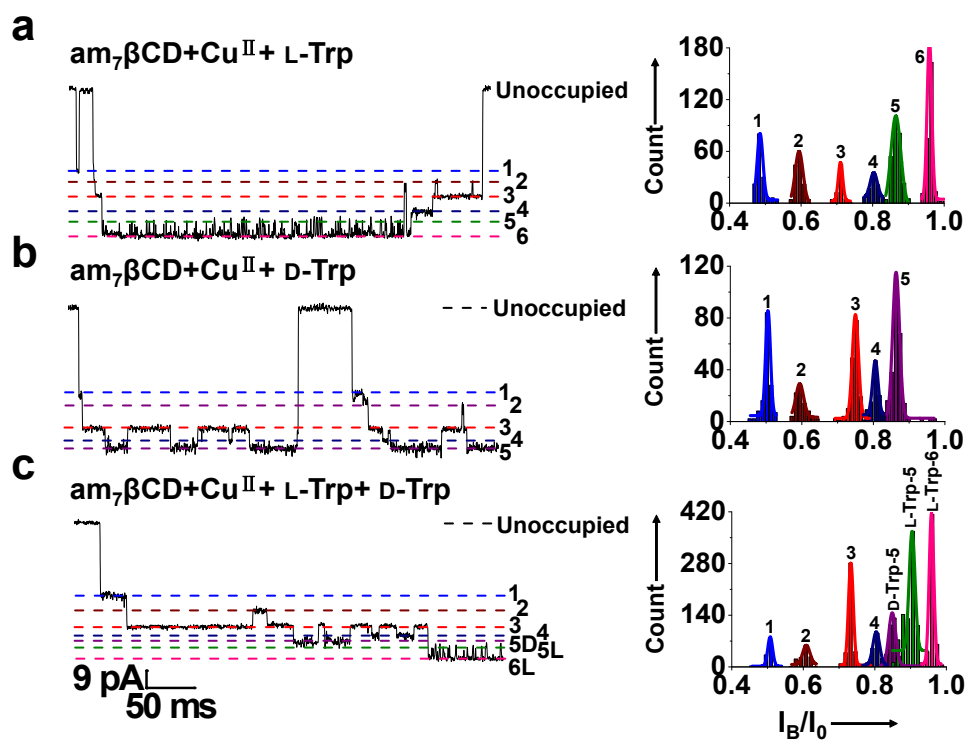


Fig. S6 Interaction of L, D-tryptophan with cyclodextrin metal complexes in (M113R)₇ nanopore. Left: representative current traces for (a) L-Trp, am₇βCD and CuCl₂; (b) D-Trp, am₇βCD and CuCl₂; (c) L-Trp, D-Trp, am₇βCD and CuCl₂. Right: the corresponding blockage current event histograms. Condition: 40 μM am₇βCD and 20 μM CuCl₂ added from the trans compartment and 20 μM L-Trp or (and) 20 μM D-Trp from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

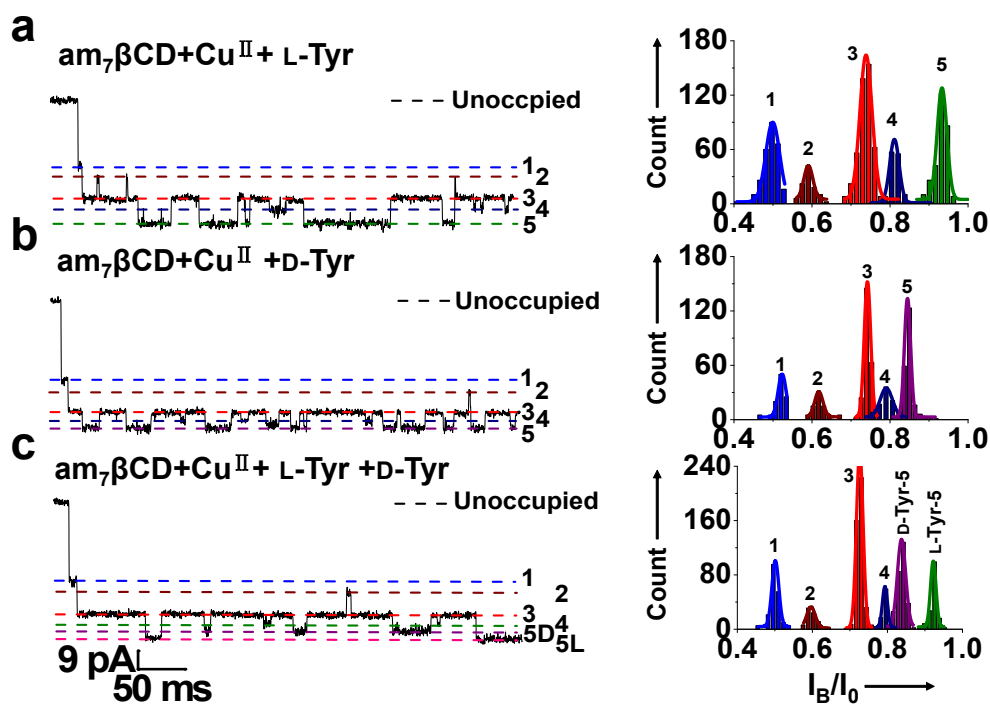


Fig. S7 Interaction of L, D-tyrosine with cyclodextrin metal complexes in (M113R)₇ nanopore. Left: representative current traces for (a) L-Tyr, am₇βCD and CuCl₂; (b) D-Tyr, am₇βCD and CuCl₂; (c) L-Tyr, D-Tyr, am₇βCD and CuCl₂. Right: the corresponding blockage current event histograms. Condition: 40 μM am₇βCD and 20 μM CuCl₂ added from the trans compartment and 20 μM L-Trp or (and) 20 μM D-Trp from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

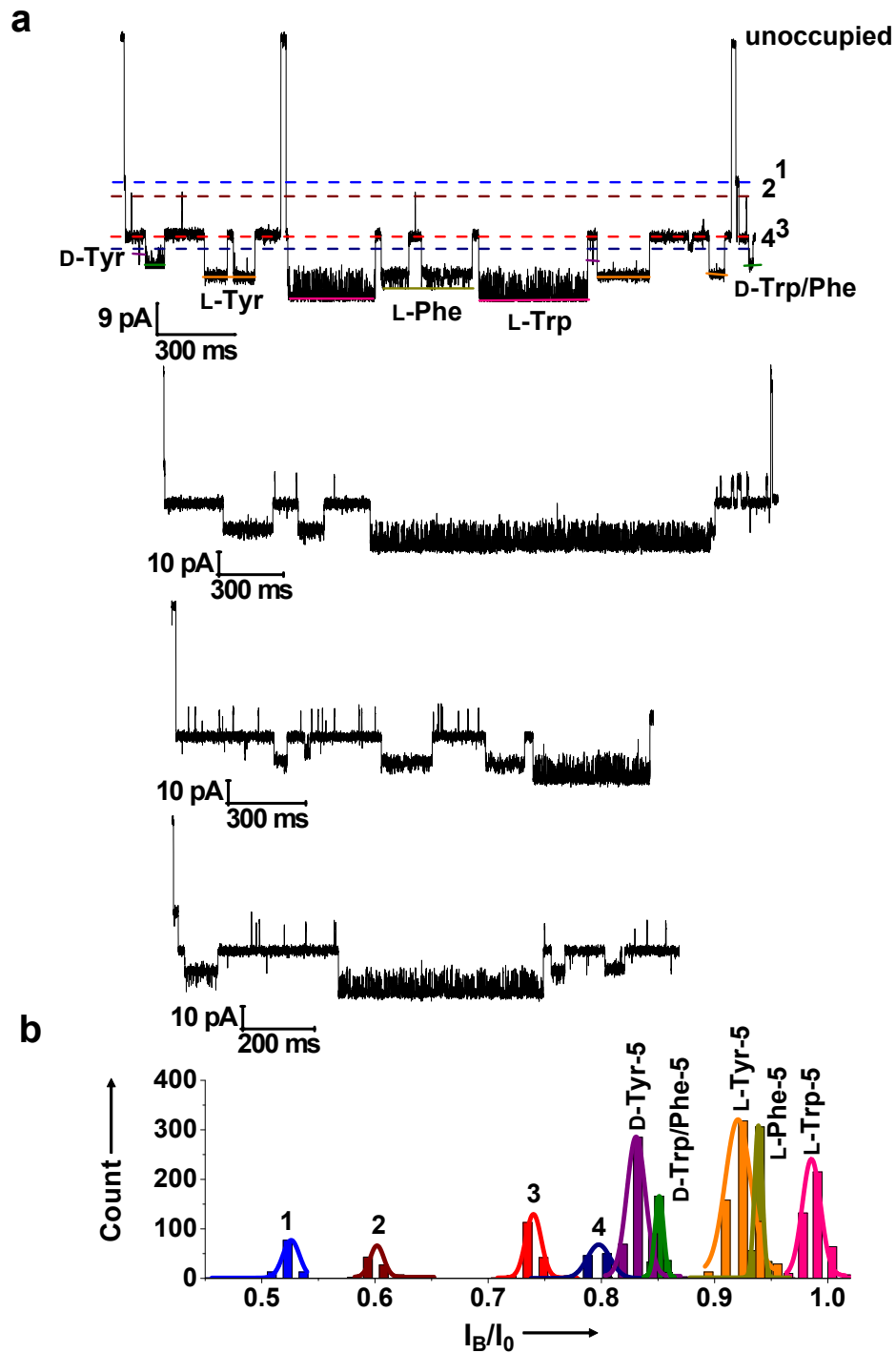


Fig. S8 Extension of the current trace of Figure 3d and the corresponding current event histogram. Condition: 40 μM am β CD and 20 μM CuCl $_2$ added from the trans compartment and a mixture of L- and D-aromatic amino acids (Phe, Trp and Tyr, 20 μM for each enantiomer) from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

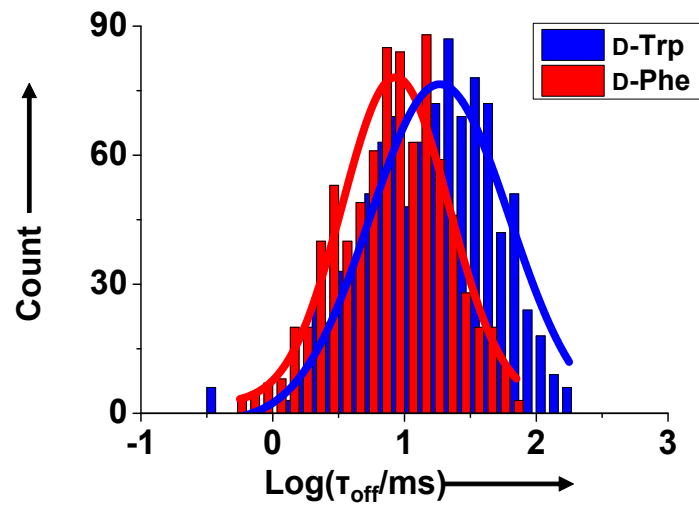


Fig. S9 The histogram of the logarithmically binned dwell time for D-Trp and D-Phe (The corresponding trace see Figure S7). The experiment conditions were the same as in Figure S8.

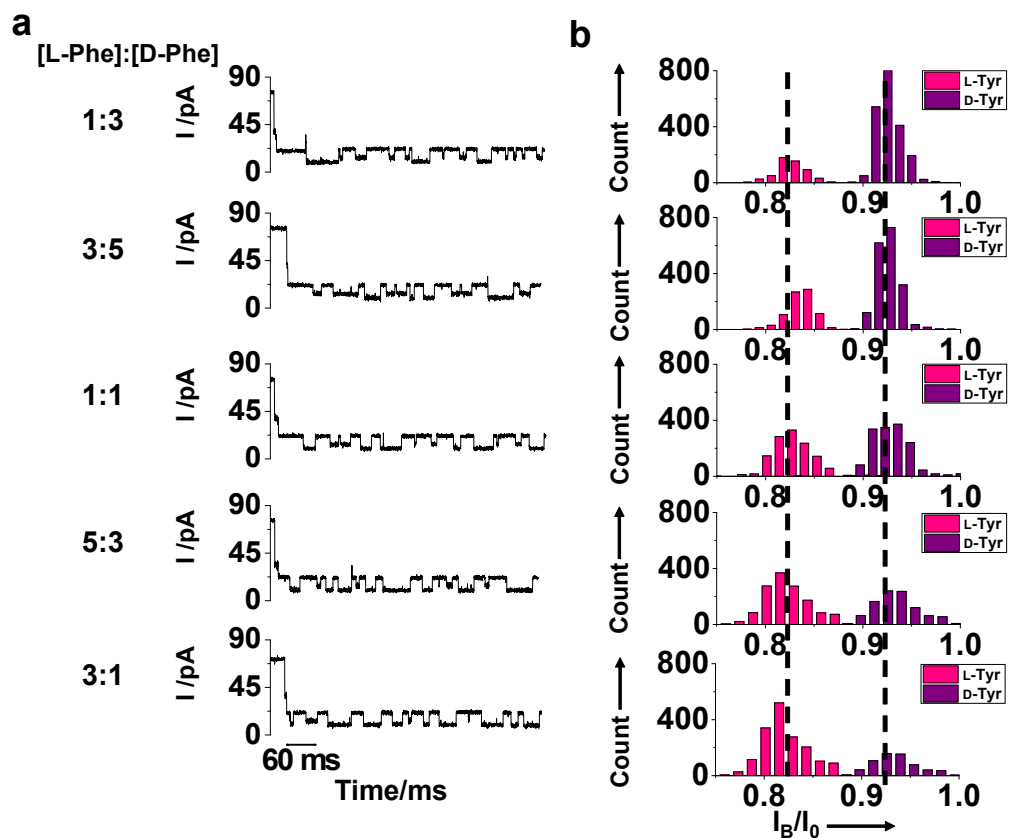


Fig. S10 Nanopore detection of enantiomeric purity in a mixture of L- and D-tyrosine. (a) Representative single channel recordings of 40 μ M tyrosine enantiomers at various L- and D-Tyr concentration ratios in the presence of 40 μ M am γ CD and 20 μ M CuCl $_2$. (b) The corresponding concentration-dependent event amplitude histograms. Condition: am γ CD and CuCl $_2$ added from the trans compartment and L- and D-Tyr from the cis side, 1 M NaCl, 10 mM MOPS, pH 8.0, +100 mV.

Table S1 The *ee* of prepared and measured for the mixtures of L- and D-tyrosine at various concentration ration. The total concentration of Tyr was fixed to 40 μ M.

[L-Tyr]:[D-Tyr]	1:3	3:5	1:1	5:3	3:1
<i>ee</i> %(Prepared)	-50.0	-25.0	0	25.0	50.5
<i>ee</i> %(Measured)	-52.3 \pm 1.7	-27.5 \pm 1.1	-3.1 \pm 0.7	25.8 \pm 1.4	52.3 \pm 2.1