Electronic supplementary information (ESI)

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

Yanli Guo, Aihua Niu, Feifei Jian, Ying Wang, Fujun Yao, Yongfeng Wei, Lei Tian and Xiaofeng Kang*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry
College of Chemistry & Materials Science
Northwest University
1 Xuefu Ave., Chang’an District, Xi’an, 710127 (P.R.China)
E-mail: kangxf@nwu.edu.cn

*Corresponding author: Prof. Xiao-feng Kang
College of Chemistry & Materials Science
Northwest University, Xi'an 710069, P. R. China
Fax: +86-029-88302604;
Tel: +86-029-88302604;
E-mail: kangxf@nwu.edu.cn
Supporting Figures and table

![Graph showing current traces](image)

**Fig. S1** Representative current traces showing no detectable current block in open and am$_7$βCD block current levels for a mixture of 20 nature L-$\alpha$-amino acids (AAS) in (M113R)$_7$ nanopore. Condition: 40 μM am$_7$βCD added from the trans compartment and a mixture of AAS (20 μM of each L-$\alpha$-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 (S$_7$βCD) as an adapter.
Fig. S2 Dwell-time histograms with exponential fits for the events arising from (a) amβCD and (b) amβCD-CuII. Experiment condition: 1 M NaCl, 10 mM MOPS buffer, pH 8.0, +100mV, 40 μM amβCD 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, amβCD and CuCl₂. (b) The corresponding blockage current event histograms. Experiment condition: 40 μM amβCD 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 μM am7βCD and 20 μM CuCl₂ added from the trans compartment and L-aliphatic α-amino acids (20 μM 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 am$_7$βCD 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, am$_7$βCD and CuCl$_2$; (b) D-Trp, am$_7$βCD and CuCl$_2$; (c) L-Trp, D-Trp, am$_7$βCD and CuCl$_2$. Right: the corresponding blockage current event histograms. Condition: 40 μM am$_7$βCD and 20 μM CuCl$_2$ 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-βCD 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 μM tyrosine enantiomers at various L- and D-Tyr concentration ratios in the presence of 40 μM am1βCD and 20 μM CuCl2.

(b) The corresponding concentration-dependent event amplitude histograms. 
Condition: am1βCD and CuCl2 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 μM.

<table>
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<th>[L-Tyr]:[D-Tyr]</th>
<th>1:3</th>
<th>3:5</th>
<th>1:1</th>
<th>5:3</th>
<th>3:1</th>
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<td>ee%(Prepared)</td>
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<td>0</td>
<td>25.0</td>
<td>50.5</td>
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