

## Electronic Supplementary Information for Chemical Communications

# Chiral Recognition of L-Tryptophan with Beta-Cyclodextrin-Modified Biomimetic Single Nanochannel

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## Experimental section

**Chemicals and Instruments:** Polyimide (PI, 12  $\mu\text{m}$  thick) (GSI, Darmstadt, Germany), sodium hypochlorite ( $\text{NaClO}$ ), potassium iodide (KI), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysulfosuccinimide (NHSS), L-tryptophan, D-tryptophan, L-histidine, D-histidine, L-phenylalanine, D-phenylalanine, L-tyrosine, D-tyrosine, potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), potassium phosphate dibasic trihydrate ( $\text{K}_2\text{HPO}_4$ ), potassium chloride (KCl), and formic acid ( $\text{HCOOH}$ ) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (SCRC, China). Mono-6-amino- $\beta$ -cyclodextrin was purchased from Sigma-Aldrich. All solutions were prepared in MilliQ water (18.2 M  $\Omega$ ). Current-voltage curves were measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH).

**Nanochannel Fabrication and Characterization:** The single conical nanochannel was prepared with a polyimide (PI, 12  $\mu\text{m}$  thick) membrane, which was irradiated with single swift heavy ions (Au) of energy 11.4 MeV per nucleon at the UNILAC linear accelerator (GSI, Darmstadt, Germany). Then the ion track polymer membrane was chemically etched at a fixed temperature (about 333 K) from one side with 13%  $\text{NaClO}$ , whereas the other side of the cell contained 1 M KI to neutralize the etchant as soon as the pore opened. After etching had finished, the film was soaked in MilliQ water (18.2 M $\Omega$ ) to remove residual salts. The diameter of the large opening (base) of the conical nanochannel was determined by scanning electron microscopy (SEM) in parallel etching experiments; the diameter  $d_{\text{tip}}$  of the small opening (tip) was evaluated

from an electrochemical measurement of the ionic conductance of the nanochannel filled with 1 M potassium chloride solution as electrolyte by means of (**Figure S1**)

$$d_{tip} = \frac{4LI}{\pi k(c)UD} \quad (1)$$

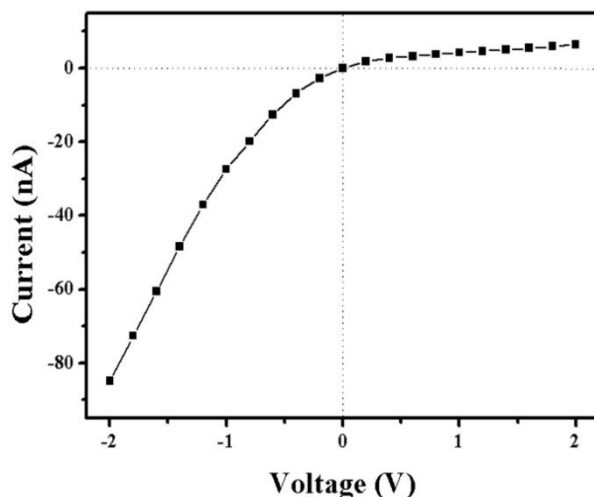
where  $d_{tip}$  is the tip diameter;  $D$  is the base diameter ( $\approx 770$  nm);  $k(c)$  is the specific conductivity of the electrolyte (for 1 M KCl solution at 25 °C  $k(c) = 0.11173 \Omega^{-1} \text{cm}^{-1}$ );  $L$  is the length of the channel, which can be approximated to the thickness of the membrane after chemical etching ( $\approx 12 \mu\text{m}$ ); and  $U$  and  $I$  are the applied voltage and measured ionic current in the pore conductivity measurement, respectively. In this work, the applied voltage and measured ionic current were 0.2 V and 1.85 nA, respectively. From **Equation (1)** and the corresponding parameters we can estimate the tip diameter of the ion track-etched nanochannel; it is around 15 nm. The etching and characterizing conductivity cell with an  $I$ - $V$  characterization of the unmodified nanochannel in the PI membrane are shown in **Figure S1**.

**Nanochannel Functionalization:** The chemical functionalization of carboxyl ( $-\text{COOH}$ ) groups generated on the channel surface during the ionic track-etching process was effected by the following procedure. The first step was the activation of these groups into amine-reactive esters by means of carbodiimide coupling chemistry. Then, these reactive esters were further condensed with CD derivatives with amino group through the formation of covalent bonds. For the activation of carboxyl groups into NHSS-ester, the PI film containing a single channel was exposed to an aqueous solution of 15 mg EDC and 3 mg NHSS for 1 h at room temperature. After they had

been washed with distilled water, the samples were further treated with 5 mM CD derivatives overnight. Finally, functionalized channels were washed several times with distilled water.

***Current–Voltage Recordings:*** The properties of the system were studied by measuring the ionic current through unmodified and modified channels. The ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single channel in the center of the PI membrane was mounted between the two chambers of the etching cell. Ag/AgCl electrodes were used to apply a transmembrane potential across the film (anode facing the base of the nanochannel), and both halves of the cell were filled with 0.2 M PB. The main transmembrane potential used in this work was a scanning voltage that varied from  $-2$  V to  $+2$  V with a period of 40 s. The process and conditions of all the measurements mentioned in this Communication were the same, unless otherwise stated, and each test was repeated 3 times to obtain the average current value at different voltages.

***Electrochemical Measurement:*** The ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). An unmodified single conical nanochannel in the center of PI membrane was mounted between two chambers of the etching cell.<sup>[1]</sup> Ag/AgCl electrodes were used to apply a transmembrane potential across the film (anode facing the base of the nanochannel), and both half of the cell were filled with 1 M KCl. The main transmembrane potential used in this work was a scanning voltage that varied from  $-2$  V to  $+2$  V with a period of 40 s.



**Fig. S1.** Ionic current was recorded at a scanning voltage varied from -2 to +2 V.

**X-ray photoelectron spectra characterization:** X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K $\alpha$  radiation. The 500  $\mu$ m X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about  $3 \times 10^{-10}$  mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. **Table S1** and **S2** showed the XPS data from PI film before and after  $\beta$ -CD modification, respectively. The changes of element content confirm the success of  $\beta$ -CD immobilization onto the surface of PI film.

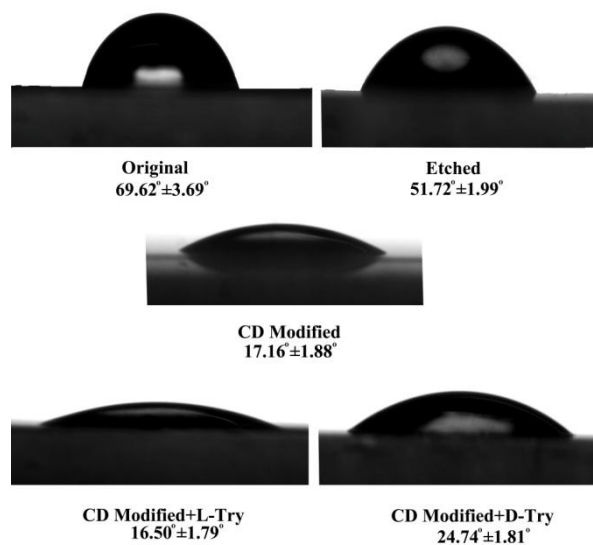
**Table S1** The XPS data from PI film before  $\beta$ -CD immobilization

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	At. %
C1s	292.67	284.81	281.02	19265.36	1.84	39274.51	64.66
N1s	404.67	400.56	396.52	2673.49	1.22	3897.93	3.97
O1s	537.42	531.87	528.23	20022.99	1.4	34392.69	21.39

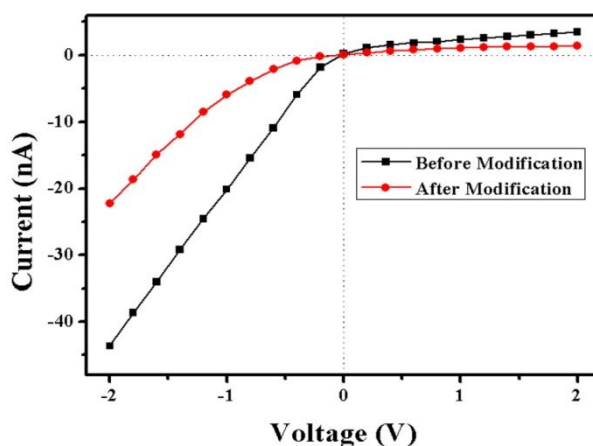
**Table S2** The XPS data from PI film before  $\beta$ -CD immobilization

Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	At. %
C1s	293.81	285.08	281.48	14234.32	2.61	41793.47	64.49
N1s	406.82	400.35	396.32	3635.08	1.43	6973.73	6.66
O1s	536.92	532.08	527.62	17988.35	2.03	39955.35	23.29

**Contact angle measurements:** Contact angles were measured using an OCA20 machine (DataPhysics, Germany) contact-angle system at ambient temperature and saturated humidity. In each measurement, an about 2  $\mu$ L droplet of water was dispensed onto the substrates under investigation. The average contact angle value was obtained at five different positions of the same sample. The original PI film for contact angle measurement was treated with NaClO (13 %) for 3 hours. The sample was then removed from the etching solution and treated with a stopping solution (1 M KI) for 30 min. After that, the sample was treated with deionized water overnight. Before the contact angle test, the sample was blown dry with N<sub>2</sub>. For the flat PI film, the mean water contact angle was  $69.6 \pm 3.7^\circ$ , becoming  $51.7 \pm 2.0^\circ$  after etching with NaClO. Once the PI film was modified with  $\beta$ -CD, the sample exhibited hydrophilic property, and the mean water contact angle decreased to  $17.2 \pm 1.9^\circ$ . After immersing into the L-Trp and D-Trp solutions, the PI film had different wettability:  $16.5 \pm 1.8^\circ$  in L-Trp and  $24.7 \pm 1.8^\circ$  in D-Trp, respectively. All these changes of wettability in PI film means the change of chemical composition.

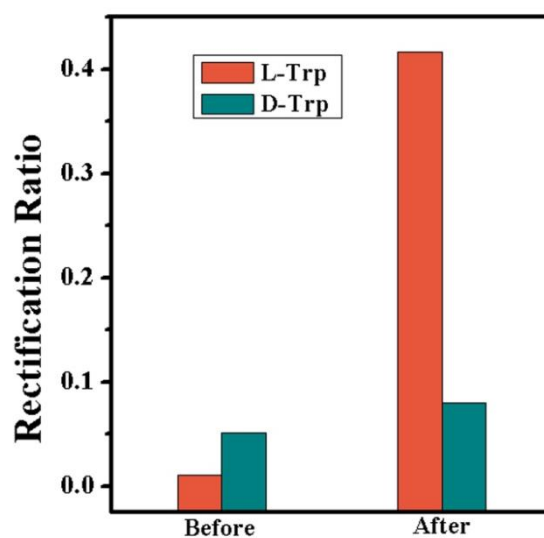


**Fig. S2.** Photographs of water droplet shape on original, etched,  $\beta$ -CD-modified,  $\beta$ -CD-modified and L-Trp-immersed, and  $\beta$ -CD-modified and D-Trp-immersed PI films with water contacting angle of  $69.6 \pm 3.7^\circ$ ,  $51.7 \pm 2.0^\circ$ ,  $17.2 \pm 1.9^\circ$ ,  $16.5 \pm 1.8^\circ$  and  $24.7 \pm 1.8^\circ$ , respectively.



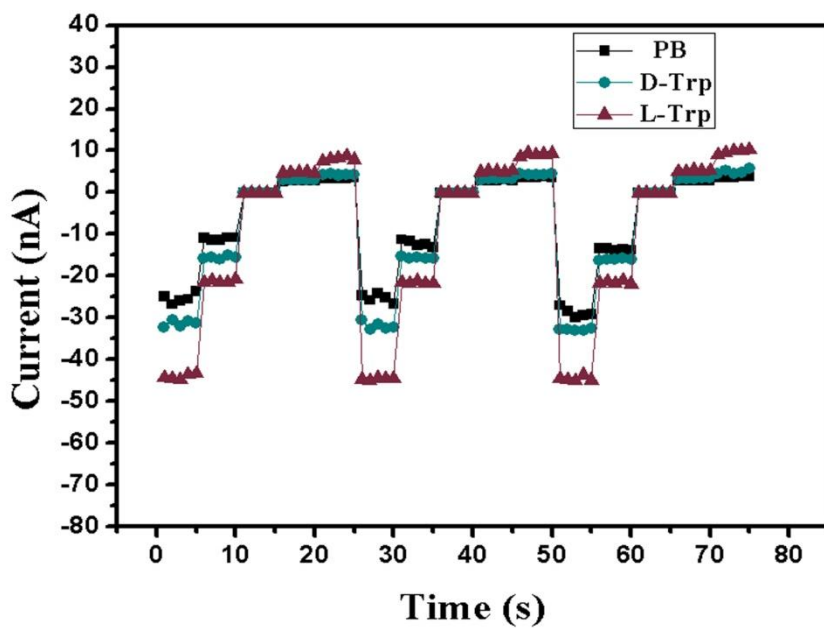
**Fig. S3.** Current-voltage ( $I$ - $V$ ) properties of the single nanochannel embedded in a PI membrane before and after  $\beta$ -CD molecules attachment onto the inner channel wall in 0.2 M PB (pH 5.9). Before functionalization, the single asymmetric nanochannel rectified the ionic current due to the presence of anionic carboxylate ( $-\text{COO}^-$ ) groups.

After modification with  $\beta$ -CD, the uncharged  $\beta$ -CD molecules diminished the negative channel surface charge, leading to a decrease in the rectified ionic current.

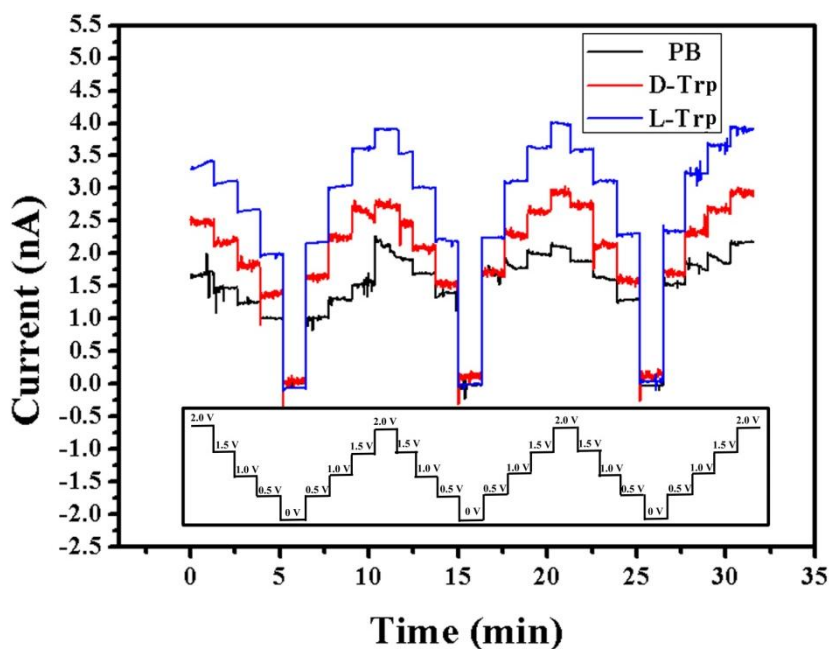


**Fig. S4.** Rectification ( $r$ ) ratio changes ( $R$ ) of this designed system before and after modifying  $\beta$ -CDs in 0.2M PB (pH 5.9) upon addition of 1 mM D-Trp or L-Trp. Rectification ( $r$ ) ratio was defined as  $(r-r_0)/r_0$ , where  $r_0$  and  $r$  are respectively rectification before and after adding D- or L-Trp. When the bare nanochannel was soaked in L-Trp solution and D-Trp solution, the value of  $R$  almost kept at 0. After modification,  $R$  of L-Trp was larger than D-Trp, which revealed the designed system can recognize L-Trp.





*Fig. S5.* Current changes with -2 V, -1 V, 0 V, 1 V and 2 V in 1 mM L-Trp and D-Trp solution. With the absolute value of voltage increasing, the ability of L-Trp recognition become stronger and stronger.



*Fig. S6.* Current changes at different positive voltages in 1 mM L-Trp solution and D-Trp solution. Each cycle included currents at 2.0 V, 1.5 V, 1 V, 0.5 V, 0 V, 0.5 V, 1 V, 1.5 V, 2.0 V.

V, 1.5 V, and 2.0 V. The larger the voltage was, the stronger the ability of L-Trp recognition was. Besides, stability is another property observed from this picture.

[1] L. Wen, Q. Liu, J. Ma, Y. Tian, C. H. Li, Z. S. Bo, L. Jiang, *Adv. Mater.* **2012**, *24*, 6193.