

Supporting Information

Porphyrin Derivative Based Tandem Response Nanochannels Triggered by Zn²⁺ and NO

**Xiao-Cui Liang,^{‡a} Shi-Qi Cheng,^{‡a} Qiang He,^a Zhong-Qiang Zhou,^a
Yanxi Zhao^{*a} and Yue Sun^{*ab}**

^a Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South-Central University for Nationalities, Wuhan 430074, P. R. China.

^b State Key Laboratory of Separation Membrane and Membrane Process; School of Chemistry, Tiangong University, Tianjin 300387, P. R. China

[‡] These authors equally contribute to this work.

Email for corresponding authors: sunyue@tiangong.edu.cn; zhaoyanxi@126.com

1. Experimental Section

1.1 Materials

Polyethylene terephthalate (PET, 12 μm thick) membranes were purchased from Germany (GSI, Darmstadt). Dichloromethane (DCM), Sodium Dodecyl Diphenyloxide Disulfonate (SDDS) Potassium Chloride (KCl), Sodium Hydroxide (NaOH), Formic Acid (HCOOH), 1-Ethyl-3-(3-dimethylaminopropyl) Carbodiimide hydrochloride (EDC $\cdot\text{HCl}$, 98%), Pentafluorophenol, Benzaldehyde ($\text{C}_7\text{H}_6\text{O}$), Boron Fluoride Ethyl Ether ($\text{BF}_3\cdot\text{OEt}_2$), 4-Acetamidobenzaldehyde ($\text{C}_9\text{H}_9\text{NO}_2$), Pyrrole ($\text{C}_4\text{H}_5\text{N}$), P-Chloranil ($\text{C}_{10}\text{H}_6\text{Cl}_4\text{O}_2$), Sulfuric Acid (H_2SO_4 , 98%), Sodium Nitrite (NaNO_2) of analytical purity were purchased from Wuhan Kejian Chemical Glass Teaching Equipment Co.

1.2 Synthesis of the Amino Porphyrin

Benzaldehyde (3.5 g, 32.87 mmol), 4-Acetamidobenzaldehyde (1.8 g, 11.23 mmol) and pyrrole (3 g, 44.7 mmol) dissolve in DCM. The mixture of dissolved solutions mixture was stirred for 15 minutes under an atmosphere nitrogen. Then 0.45 mL of 2.5 M $\text{BF}_3\cdot\text{OEt}_2$ were added 1.5 h at room temperature and added P-Chloranil (2.3 g, 9.35 mmol). After the mixture was reacted for 15 h at room temperature. The reaction solution was concentrated at reduce pressure and the crude product was purified by silica gel column chromatography using DCM to obtain purple powder (56%). $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.96 (d, $J = 4.4$ Hz, 2H), 8.79 (s, 6H), 8.20 (dd, $J = 5.4, 2.1$ Hz, 6H), 7.87 (d, $J = 8.3$ Hz, 9H), 7.04 (dd, $J = 23.3, 7.2$ Hz, 2H), 5.75 (s, 2H).

1.3 Bullet Nanochannels Fabrication

PET membrane was irradiated with an energetic heavy metal ion beam to form single cylindrical pores. Then, electrochemical etching technique was used to obtain bullet nanochannels. Before etching, the membranes were irradiated under UV light (365 nm) for 2 h from both sides, respectively. Then, the PET membrane was chemically etched at a stationary temperature (65 °C) with etching solution (6 M NaOH) on one side, (6 M NaOH and 0.025% (SDDS) on the other side and Pt as electrodes. Stop solution with 1 M KCl and 1 M HCOOH both side membrane. After the etching process, the residual salts were removed by washing with deionized water several times. Bullet nanochannels were successfully constructed. The diameter and shape of the nanochannels were determined using scanning electron microscopy (SEM), the large opening (base) was about 282 nm, and the tip was calculated about 45 nm.

1.4 Chemical Modification

The carboxyl (-COOH) groups were generated on the bullet channel surface during the ion track-etching process. The PET nanochannels surface was activated by 30 mg EDC • HCl and 6 mg pentafluorophenol placed into a culture dish for 1 h. Then ATPP (10^{-2} M) and Zn^{2+} (10^{-2} M) solution was sequentially modified onto the inner surface of the nanochannels to obtain the functional nanochannel.

1.5 Current Voltage Measurement

The ionic current before and after modification channels was measured by a Keithley 6487 Picoammeters. A bullet nanochannel membrane was mounted between two chambers of the cell. Ag/AgCl as electrodes and scanning voltage varied from -2

to +2 V at 0.1 M KCl solution were used to measure the ion current. The I-V curves were recorded before and after modification with ATPP, subsequent modification with Zn²⁺ and further bubble of NO, respectively.

1.6 Electroosmotic Flow (EOF) Tests

A porous PET membrane after etching was used to test EOF experiment and calculate the surface charge density.¹ Phenol (0.01 mM) served as feed permeate was added the side tip of the cells, the base side of the cell was added KCl (0.1 mM) as permeate. Fluorescence intensity of the permeation solution measured with a fluorescence 11 spectrometry system. Test the fluorescence at an interval of 30 minutes and accumulated 150 minutes. Two contrasting test methods was performed, no voltage was applied, voltage was applied, respectively.

1.7 Surface Charge Density Calculation

The permeate experiment of phenol is tested in the absence of applied current to determine the rate of diffusion (N_{diff}). N_i is the transport of phenol at +2 V (the rate with applied current). Thus, the enhancement factor (E) can be obtained by the supplementary equation:

$$E = N_i / N_{diff} \quad (1);$$

Peclet number (Pe) can be determined (Eq. (2)) as,

$$E = Pe / (1 - e^{-Pe}) \quad (2);$$

The relationship between Pe and V_{eof} is determined using Eq. (3) as,

$$V_{eof} = Pe \times D/L \quad (3);$$

$$V_{eof} = -\epsilon \zeta J_{app} \rho / \eta \quad (4);$$

Surface charge density (σ) using Eq. (5) as,

$$\sigma = \varepsilon \zeta / K^{-1} \quad (5).$$

Analogous experiments were completed to determine N_{diff} (the rate of diffusion in the absence of applied current and N_i (the rate with applied current), D is the diffusion coefficient for phenol ($D = 8.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and L is the membrane thickness ($L = 12 \mu\text{m}$). The ζ potential of the nanochannel walls can be determined (Eq (4)) (ε and η are the permittivity and viscosity of the solution, respectively, $\varepsilon = 6.95 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$, $\eta = 0.89 \text{ cp}$; J_{app} is the constant applied current density; ρ is the resistivity of the electrolyte within the nanochannel, $\rho = 2.23 \text{ K}\Omega$). We may extract the ζ and then surface charge density values can be estimated from the Gouy-Chapman equation (K^{-1} is the effective thickness of the electrical double layer, $K^{-1} = (9.61 \times 10^{-9}) (z^2 c)^{-1/2}$) (Eq. (5)).

1.8 Structural Characterizations

The morphology of PET characterized by Field-Emission Scanning Electron microscopy (FESEM) (HITACH SU8010). Chemical element composition was measured by X-ray Photoelectron Spectroscopy were carried out using a XPS spectrometer (Escalab 250Xi, Thermo Scientific), The contact angle image of the PET member was obtained using an optical contact angle measuring instrument (KRUSS, DSA100). The ion currents and sweep voltages (-2 V/+2 V, 0.1 V/s) were measured by a Picoammeter Keithley 6487. ^1H NMR spectra was recorded on a Bruker Avance DMX 400 spectrophotometer (Germany).

2. Supplementary Figures

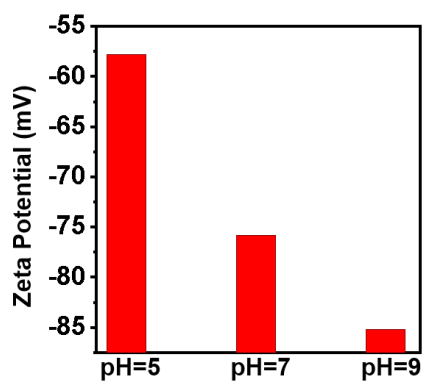


Figure S1. Zeta potential of the bare nanochannel under different pH.

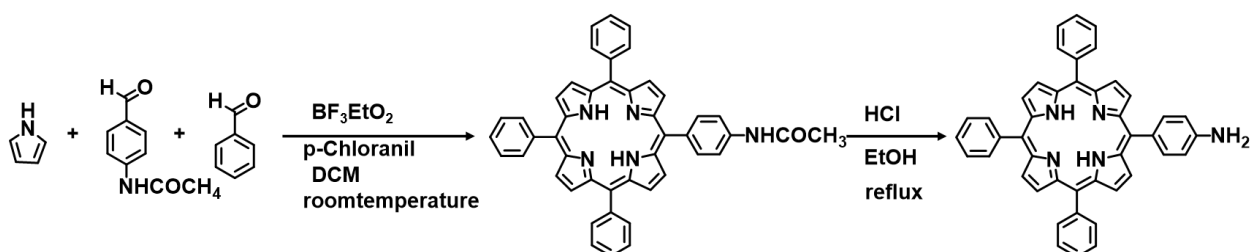


Figure S2. Synthesis of amino porphyrin route.

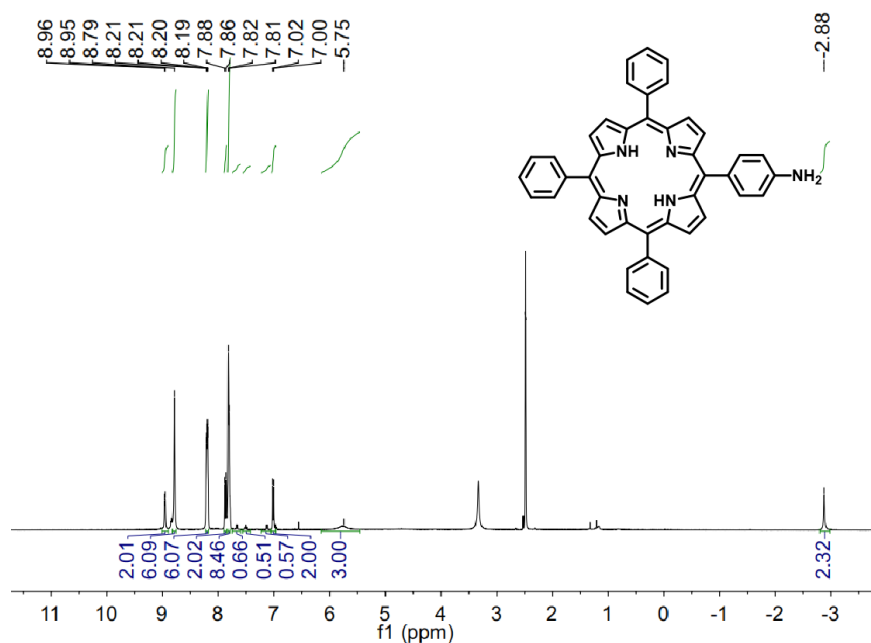


Figure S3. ^1H NMR (400 MHz, DMSO) of amino porphyrin.

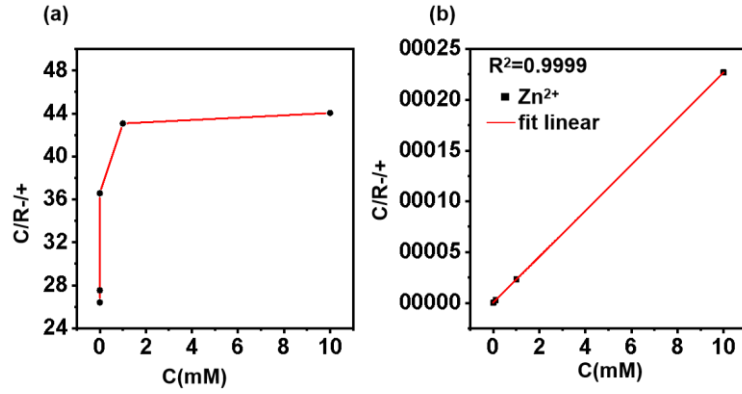


Figure S4. (a) The change in $R_{-/+}$ of the ATPP-based nanochannel in the presence of different concentrations of the Zn^{2+} . (b) Langmuir isotherm plots the linear relation of $C/R_{-/+} - C$.

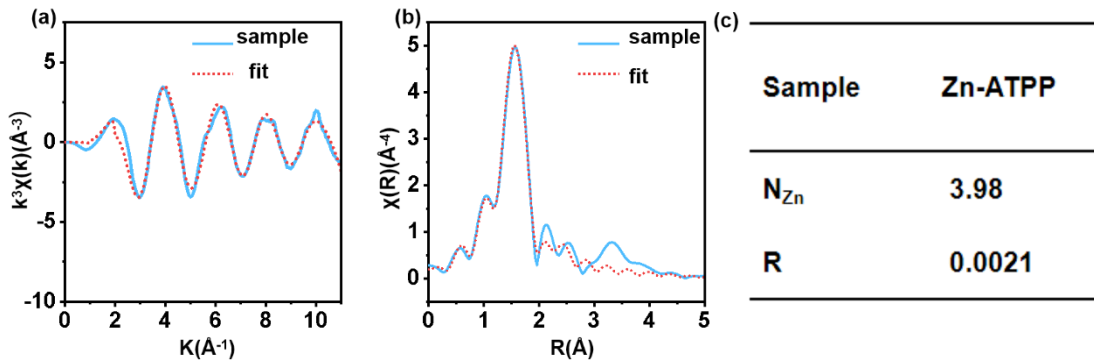


Figure S5. (a) Zn k-edge EXAFS spectra (solid blue lines) and corresponding theoretical fitting curve (dotted lines). (b) Fourier transforms of Zn k-edge EXAFS spectra. (c) Parameters obtained from fitting the EXAFS spectra: coordination numbers for the first (N_{Zn}), R-Factor for the respective fit.

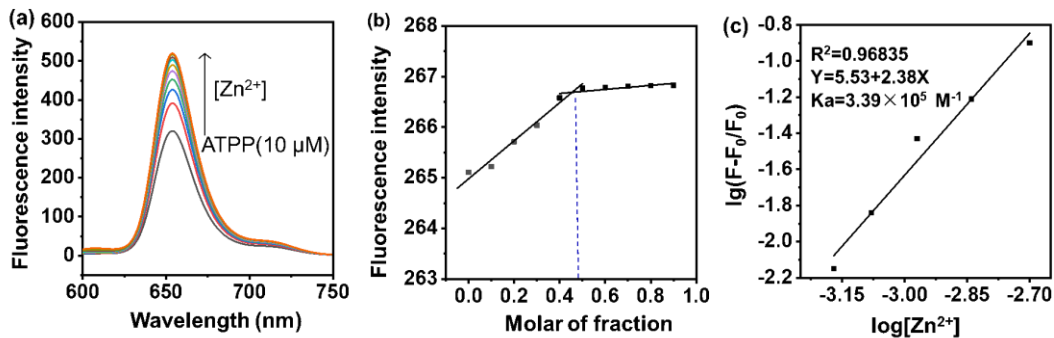


Figure S6. (a) Fluorescent titration experiment of porphyrin in methanol toward the various concentrations of Zn^{2+} . (b) The job's plot for porphyrin and Zn^{2+} . (c) The binding constant (K_a) between porphyrin and Zn^{2+} . Plot of $\log [(F - F_0)/F_0]$ as a function of the $\log C_{Zn(II)}$ F_0 and F are the fluorescence intensity of ATPP (1.0×10^{-5} mol/L).

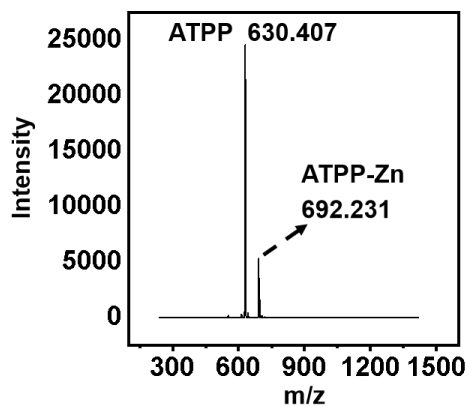


Figure S7. The mass spectrometry of an equimolar mixture of ATPP and Zn^{2+} .

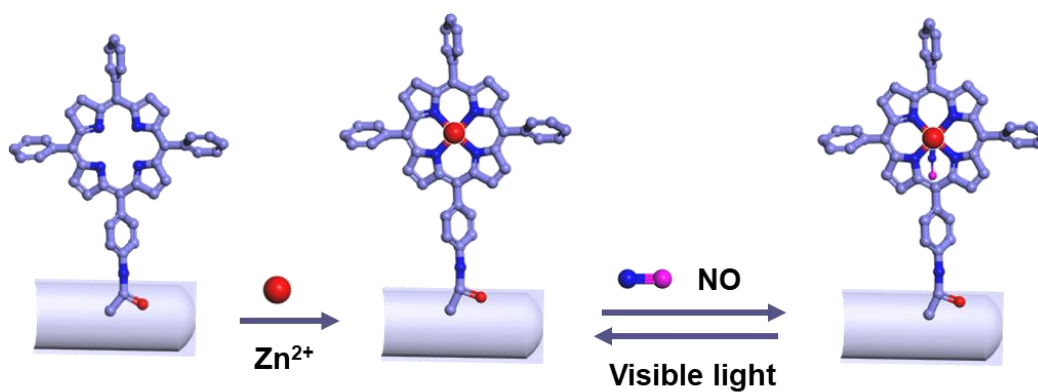


Figure S8. The tandem response nanochannels triggered by Zn^{2+} and NO with good reversibility.

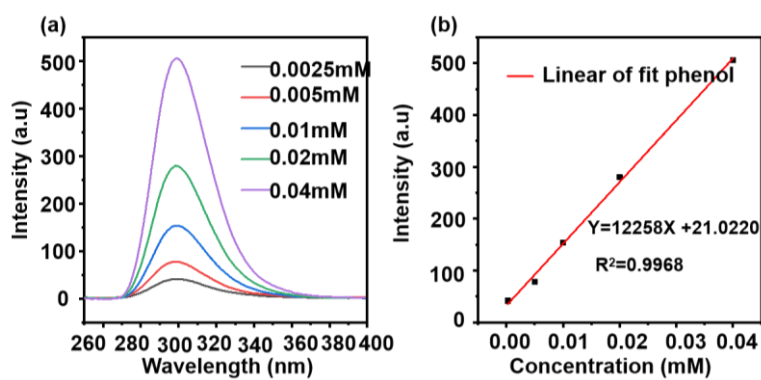


Figure S9. (a) Fluorescence absorption of phenol at different emission wavelengths. (b) Standard curve of phenol.

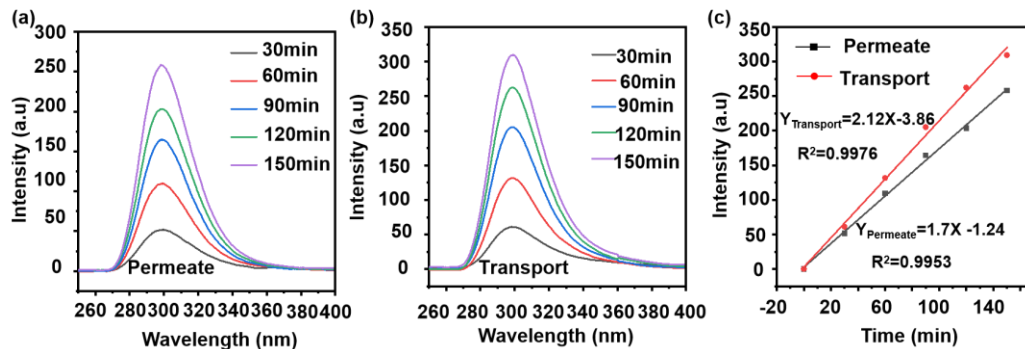


Figure S10. (a) The phenol permeates in the bare bullet-shaped nanochannel. (b) The phenol transports in the bare bullet-shaped nanochannel under the voltage (+2 V). (c) The calculated surface charge density (σ) in the bare bullet-shaped nanochannel.

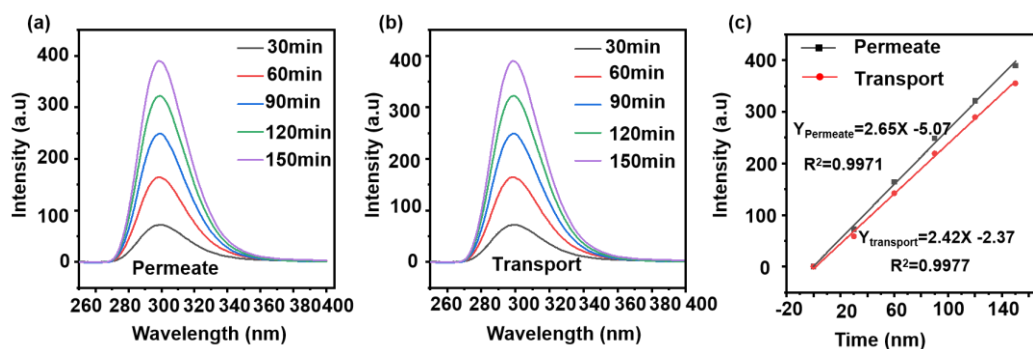


Figure S11. (a) The phenol permeates in the modified with ATPP bullet-shaped nanochannel. (b) The phenol transports modified with ATPP bullet-shaped nanochannel under the voltage (+2 V). (c) The calculated surface charge density (σ) in the ATPP bullet-shaped nanochannel.

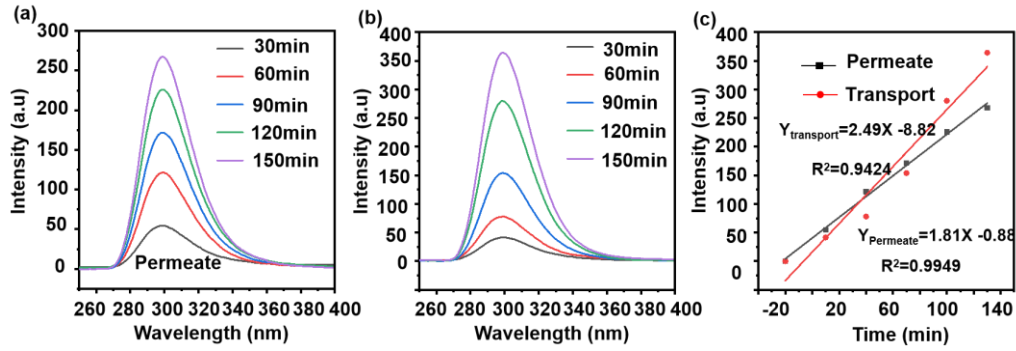


Figure S12. (a) The phenol permeates modified with Zn^{2+} bullet-shaped nanochannel. (b) The phenol transports modified with Zn^{2+} bullet-shaped nanochannel under the voltage (+2 V). (c) The calculated surface charge density in the Zn^{2+} bullet shaped nanochannel.

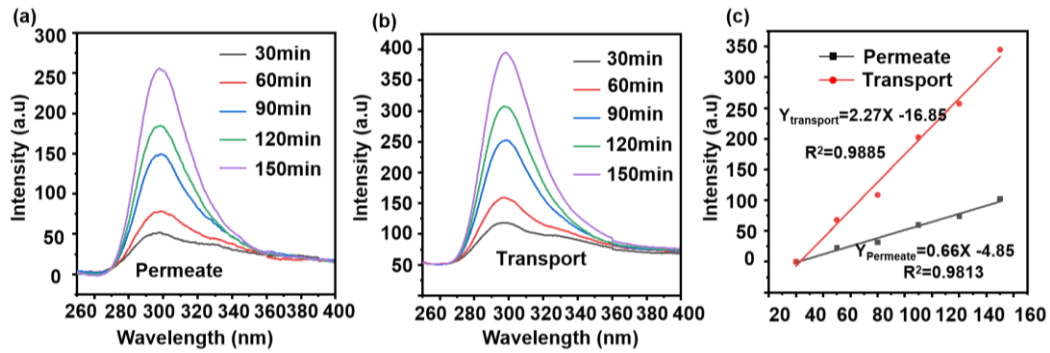


Figure S13. (a) The phenol permeates in the modified with NO bullet-shaped nanochannel. (b) The phenol transports modified with NO bullet-shaped nanochannel under the voltage (+2 V). (c) The calculated surface charge density (σ) in the NO bullet-shaped nanochannel.

	Japp (mA cm ⁻²)	Veof (cm s ⁻¹)	σ (e nm ⁻²)
Bare-bullet-shaped nanochannel	-0.37	3.4*10 ⁻³	-0.0415
APP-bullet-shaped nanochannel	0.29	1.4*10 ⁻³	-0.0312
Zn ²⁺ -bullet-shaped nanochannel	-0.32	5*10 ⁻³	-0.0898
NO-bullet-shaped nanochannel	0.26	3.7*10 ⁻³	-0.0423

Table S1. The inner surface charge density (σ) of the functionalized bullet-nanochannels with modified bare, ATPP, Zn²⁺ and NO, respectively.

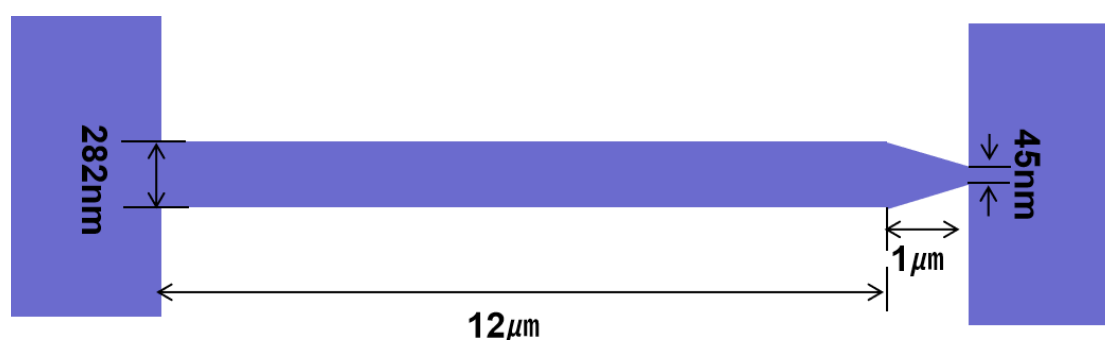


Figure S14. The model of numerical simulation about bare nanochannel. The model column and cone length are 11 μm and 1 μm, respectively. The base side diameter of is 282 nm, and 45 nm (tip side). The surface charge density of bare, ATPP, Zn²⁺ and NO functionalized nanochannel are measured by EOF experiments. Applied +2 V potential at the base side as a driving force to demonstrate the ion behavior.

3. References

1. M. Cheng, F. Zhu, S. Y. Zhang, X. R. Zhang, M. K. Dhinakaran, and H. B. Li, *Nano. Lett.*, 2021, **21**, 4086-4091.