



Supporting Information

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Phosphate-Responsive Biomimetic Nanofluidic Diodes
Regulated by Polyamine–Phosphate Interactions: Insights into
Their Functional Behavior from Theory and Experiment

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Phosphate-responsive biomimetic nanofluidic diode regulated by polyamine-phosphate interactions. Insights into their functional behavior from theory and experiment.

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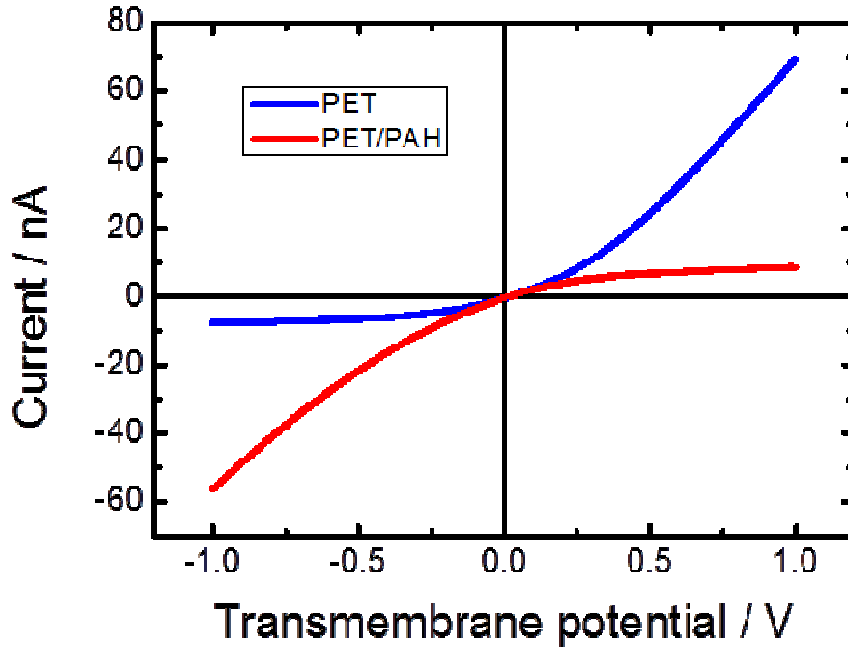


Figure S1. *I-V curves for a bullet-like nanochannel before and after the modification with PAH.*

Poisson-Nernst-Planck model

The set of equations used to model the transport through nanochannels are, Nernst-Planck equations,

$$\vec{J}_i = -D_i(\nabla c_i + z_i c_i \nabla \phi) \quad (1)$$

The Poisson Equation,

$$\nabla^2 \phi = -\frac{F^2}{\epsilon RT} \sum_i z_i c_i \quad (3)$$

And the continuity equation,

$$\nabla \cdot \vec{J} = 0 \quad (4)$$

Where \vec{J}_i , D_i and z_i are, the ionic flux, the diffusion coefficient, the ion charge of specie i , respectively. ϵ is the permittivity of the solution inside the channel.

Approximation: one-dimension model

Taking into account that the channel is very large, we can make the following assumptions¹

- 1) The flow is only in the axial direction, so we can write Nernst-Planck and the continuity equations as,

$$J_i = -D_i \left(\frac{dc_i}{dx} + z_i c_i \frac{d\phi}{dx} \right) \quad (5)$$

$$\frac{d}{dx} (\pi a^2 J_i) = 0 \quad (6)$$

Here, a is the nanopore radius that is determined by

$$a(x) = \frac{a_R - a_L \exp[-(d/h)^n] - (a_R - a_L) \exp[-(x/d)^n (d/h)^n]}{1 - \exp[-(d/h)^n]} \quad (7)$$

$n > 0$

n and d/h are geometrical parameters that determine the shape of the pore.

- 2) If the nanochannels are very large, we can use the electroneutrality condition instead the Poisson equation.

$$\sum_i z_i c_i + X_F = 0 \quad (8)$$

Where X_F is the concentration of the fixed charges that is defined as,

$$X_F = \frac{2\sigma}{aF} \quad (9)$$

Where σ is the surface charge density.

At the borders we assume Donnan equilibrium,

$$c_i(0) = c_L \exp(-z_i \Delta\phi_L) \quad (10a)$$

$$c_i(d) = c_R \exp(z_i \Delta\phi_R) \quad (10b)$$

Where,

$$\Delta\phi_L = \phi(0) - \phi_L \quad (11a)$$

$$\Delta\phi_R = \phi_R - \phi(d) \quad (11b)$$

Solving these equations we obtained the average potential and concentration profiles of each species. From these we could calculate the current in any section of the nanopore as,

$$I = \sum_i z_i F \pi a^2 J_i \quad (12)$$

Parameters used for the model

$$\sigma = 1.5 \text{ lel/ nm}^2$$

$$\text{Diameter}_{\text{base}} = 450 \text{ nm}$$

$$d/h = 15$$

$$n = 1$$

Using these parameters to fit the experimental curves, a tip diameter of 35 nm was obtained.

A concentration of 0.1 M for both K and Cl was used. The concentration for phosphate ions was changed to match each experiment. The relation between dihydrogen phosphate (1) and hydrogen phosphate ions (2) was calculated assuming that at pH 7, 39 % of the phosphates are in state (1) and a 61 % as (2). Table S1 shows the diffusion coefficients used for the simulations.

Ion	Coef (/10 ⁻⁵ cm/s)
K ⁺	1.957
H ₂ PO ₄ ⁻	0.959
Cl ⁻	2.03
HPO ₄ ⁻²	0.759

Table S1. Diffusion coefficients used for each ionic species.

Monte Carlo Simulations

MC simulations were used to obtain the radial distributions of ionic species for a 10 nm nanopore with and without surface charge.

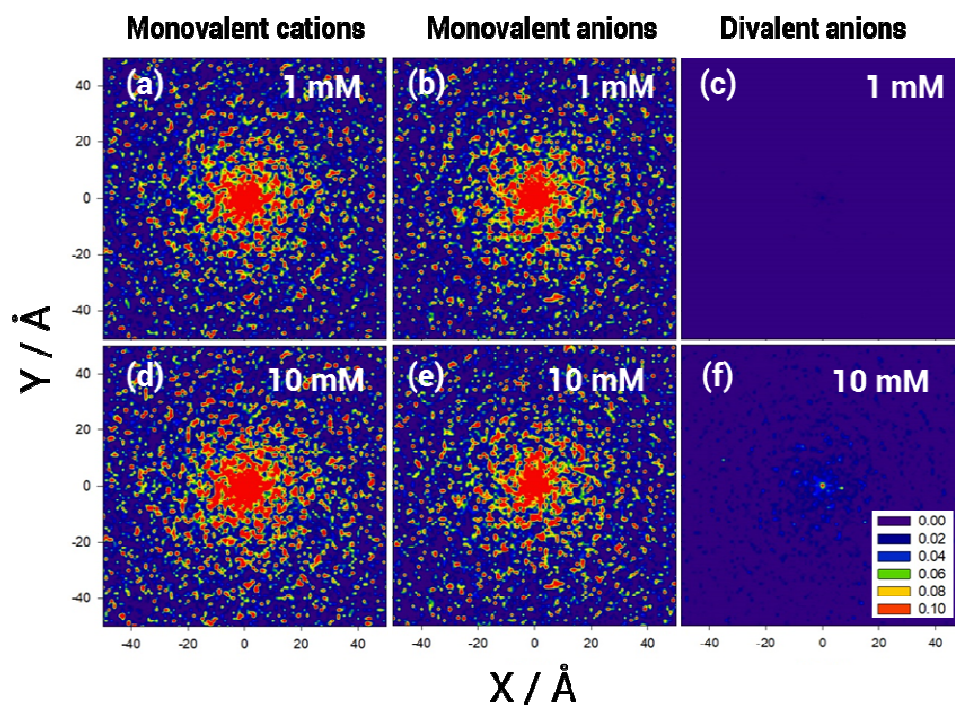


Figure S2. 2D Ionic distribution inside a 10 nm-diameter bare channel without charge over the walls at a divalent salt bulk concentration of (a), (b), (c) 1 mM and (d), (e), (f) 10 mM.

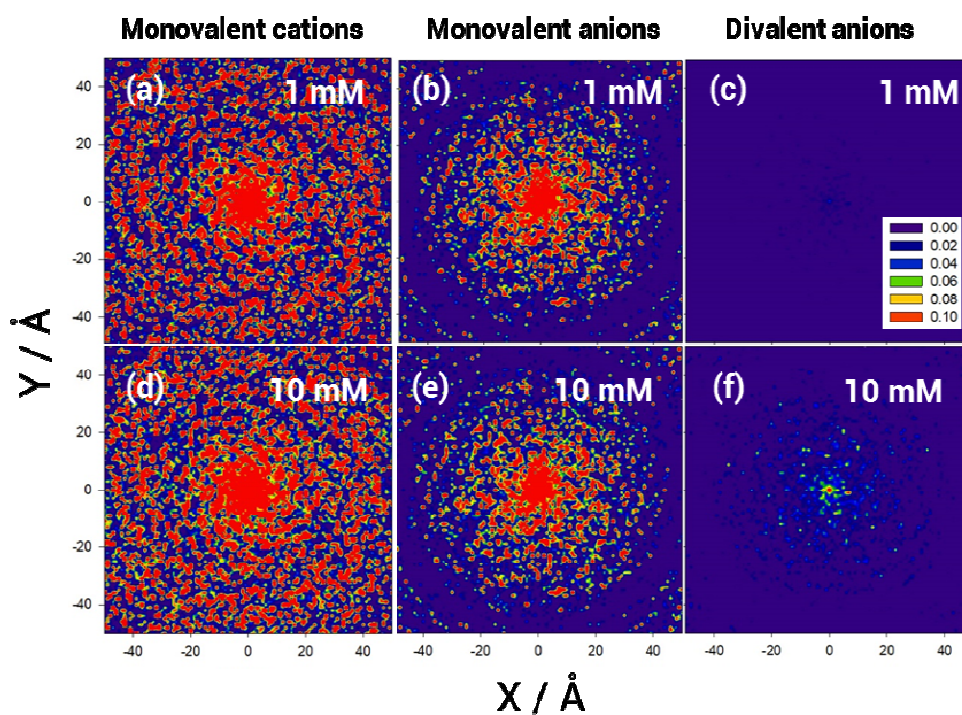


Figure S3. 2D Ionic distribution inside a 10 nm-diameter bare channel and charged at the walls at a divalent salt bulk concentration of (a), (b), (c) 1 mM and (d), (e), (f) 10 mM.

Zeta potential measurements

Experimental

Chemicals

Polyallylamine hydrochloride (PAH) (ca. 58 kDa) was purchased from Sigma-Aldrich. The pH of stock solutions of PAH (1 mg ml^{-1}) was adjusted to 7 by adding 10% KOH. KH_2PO_4 was from Carlo Erba. Ethanol and NH_4OH were purchased from Anedra, tetraethyl orthosilicate (TEOS) and HEPES was from Sigma-Aldrich.

All chemicals were of analytical grade. The water used in all experiments was purified by a Millipore system and its resistivity was $18.2 \text{ M}\Omega \text{ cm}$.

Silica Particles synthesis

Silica particles (SP) were synthesized by the Stöber method.² Briefly, 20 ml ethanol and 5.5 ml NH_4OH were mixed under magnetic stirring. Then 1 ml TEOS was added and the solution was stirred for 60 min at 30°C . The reaction solution was then centrifuged to separate the SP, which were successively re-dispersed and centrifuged employing ethanol and water as washing solvents.

For functionalization, the SPs were dispersed in 0.1 M KCl 1 mg ml^{-1} PAH solution and stirred for 30 min to allow the adsorption of the polyelectrolyte. The SPs were then centrifuged and washed twice with 0.1 M KCl in $0.5 \text{ mM pH } 7$ HEPES buffer.

Size and ζ -potential measurements

The size of the SPs was determined by DLS employing a Zetasizer Nano (Nano ZSizer-ZEN3600, Malvern, U.K.) in water at 25°C employing a distribution fitting method. The size of the unmodified SPs was determined to be $780 \pm 140 \text{ nm}$. The ζ -potential of the colloidal SPs was determined from the electrophoretic mobility measured by Laser Doppler Velocimetry with a Zetasizer Nano (Figure S2). The Smoluchowski approximation of the Henry equation was employed for calculations. Measurements were performed in triplicate using disposable capillary cells (DTS 1061 1070, Malvern) at 25°C with a drive cell voltage of 30 V and employing the monomodal analysis method. The ζ -potential of unmodified SPs in 0.1 M KCl in $0.5 \text{ mM pH } 7$ HEPES buffer was $-27 \pm 2 \text{ mV}$.

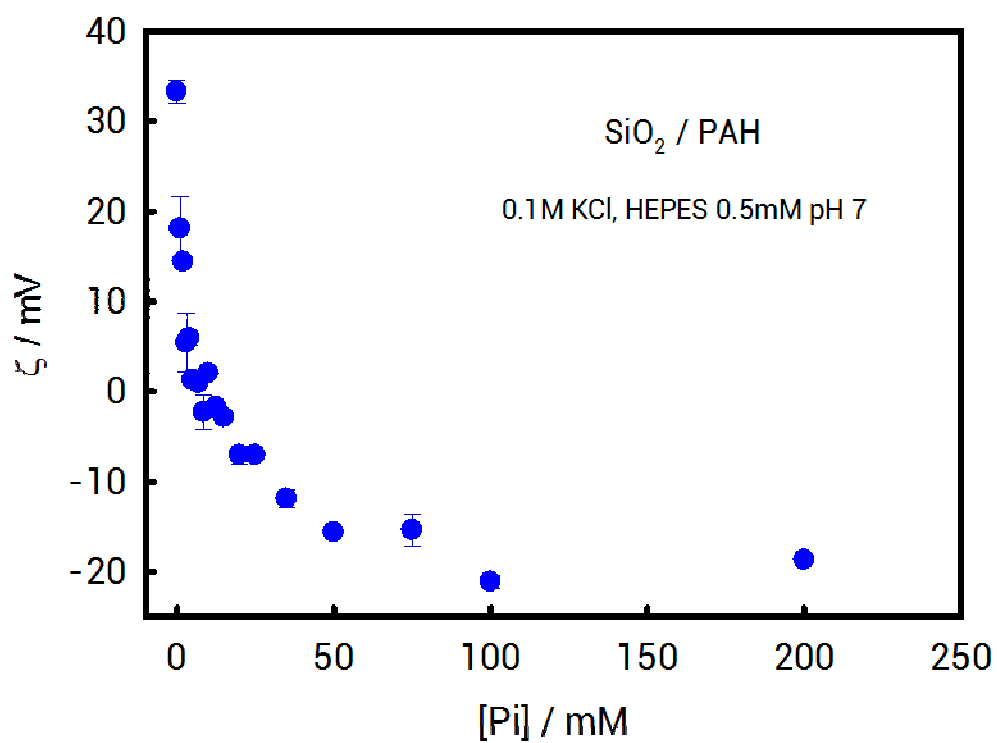


Figure S2. Zeta potential versus total phosphate concentration for PAH-modified silicon dioxide nanoparticles.

References

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- ¹ Ramírez, P., Apel, P. Yu., Cervera, J., Mafé, S. *Nanotechnology*, **2008**, *19*, 315707.
² Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.