We simulate 16 chains that are grafted in a square array and periodically replicated along the $x$- and $y$-directions. The system (main text Figure 1) has dimensions $[0, L] \times [0, L] \times [0, L_z]$, where $L$ is adjusted to vary the grafting density and $L_z = 12.5\sigma$. The actual simulation cell extends from $z = -L_z$ to $z = L_z$ to accommodate the image charges. Electrostatic interactions are calculated via a modified three-dimensional particle–particle particle–mesh algorithm\(^1\) with relative accuracy $10^{-5}$. Artifacts owing to the periodicity in the $z$-direction are suppressed by adding a $4L_z$-thick vacuum layer and a dipole correction.\(^2\) We confirmed that this reduces the systematic relative root-mean-square error in the force on each ion to less than $10^{-7}$, significantly smaller than
the precision of the electrostatic solver. The solvent viscosity opposing the ion motion is captured by a Langevin thermostat with damping time $\tau = (m\sigma^2/\epsilon_{LJ})^{1/2}$ is the LJ unit of time. We equilibrate the system for $10^6$ steps (of length $0.01\tau$) after which we continue with production runs for $10^8$ steps, corresponding to $5.6\ \mu s$. By comparison, the long runs for simple electrolytes in Ref. 3 correspond to $0.056\ \text{ms}$ (not 5.6 ms as erroneously stated). Simulations were conducted using a version of LAMMPS$^4$ that was modified to account for image charges.

Figure S1: Ion transport and brush structure as a function of external driving field. (a) Ion mobility $\mu = \langle v \rangle / (Eq)$ and the brush height $H_b = (\int_0^{L_z} \rho_b(z) z \, dz) / (\int_0^{L_z} \rho_b(z) \, dz)$ as a function of the external electric field $E$. As the field strength is increased, the ion response becomes nonlinear. Both the onset and the magnitude of this nonlinearity depend on brush grafting density, with a slightly earlier and stronger deviation for a sparse brush, where ion transport is dominated by electrostatic ion–polymer binding. A sparse brush is also capable of larger deformation under an external field, as reflected in the more pronounced response of the brush structure (Figure S1b), which in turn also affects ion response. Based on these data, we choose to utilize a low driving field of magnitude $E = 0.02\epsilon_{LJ}/(\sigma e)$ to obtain the results presented in the main text.
Figure S2 summarizes how the effects of surface polarization on ion mobility (top row), counterion distribution (middle row), and monomer distribution (bottom row) change when the brush grafting density $\Gamma$ is varied. The counterion distributions and the polymer distributions are normalized (unlike in Figure 3b in the main text) to illustrate the relative magnitude of the dielectric effects at different $\Gamma$.

For all the quantities presented in Figures S2, both the magnitude and range (in terms of distance to the substrate) of the dielectric modulation are reduced when $\Gamma$ is increased. This can be understood from the increase in electrostatic screening at larger $\Gamma$. This screening, along with the decreased importance of electrostatic interactions for ion transport at high $\Gamma$, explains why the ion mobilities become independent of substrate permittivity in dense brushes (Figure 3a, main text).

The relative magnitude of the perturbation caused by substrate permittivity on local mobility (Figure S2, top) is always comparable for $\Delta = -1$ and $\Delta = 1$. This indicates that the stronger modulation of the average ion mobilities (Figure 3a, main text) by a conducting substrate must stem from the build-up of ions owing to the attractive polarization.

Unlike the comparable modulation of local mobilities for $\Delta = \pm 1$, the dielectric effect on the spatial distribution of charge is strongly asymmetric. A high-permittivity substrate causes a more pronounced change in both the ion and the polymer distributions than a low-permittivity substrate. The polymer distribution (Figure S2, bottom row) reveals that this originates from the grafting of the polymers to the interface: the monomers cannot be fully repelled by the insulating substrate—a constraint which then propagates to the ion distribution (Figure S2, middle row) via ion–monomer binding (the results shown are obtained at Manning parameter $\xi \approx 2.67$). Note that the comparable modulation of local mobilities for $\Delta = \pm 1$ also indicates that the small modifications of polymer and ion densities caused by the surface polarization are not strong enough to have an effect on the mobilities via electrostatic screening or steric effects.

Above (Figure S2) and in the main text Figure 3a, we have truncated the mobility and distribution profiles at the distance $z = 3\sigma$ to focus on the dielectric effects occurring at the interface. The profiles with the full $z$-range are presented in Figure S3 for the same system as in Figure 3b in
Figure S2: Range and magnitude of the dielectric effects for different grafting densities. Ion mobility $\mu$, normalized counterion density distribution $\rho_c^*$ (rescaled by the overall counterion density), and normalized brush monomer density distribution $\rho_b^*$ (rescaled by the overall monomer density) are presented as a function of the distance to the substrate for grafting densities (a) $\Gamma = 0.01 \sigma^{-2}$, (b) $\Gamma = 0.02 \sigma^{-2}$, and (c) $\Gamma = 0.04 \sigma^{-2}$. The effect of the substrate permittivity on local mobilities is almost equally strong for $\Delta = -1$ and $\Delta = 1$, whereas the effect on local ion and polymer densities is much stronger for $\Delta = -1$ than for $\Delta = 1$. As grafting density increases, the dielectric modulation of all quantities presented diminishes due to electrostatic screening.

Figure S4 summarizes the effects of changing the Manning parameter $\xi = l_B \lambda$ on ion mobility, brush structure, and ion flux. We vary $\xi$ either by changing $l_B$ (variation of solvent permittivity or temperature) or by scaling the monomer charges (variation of $\lambda$). The functional dependence of
Figure S3: Ion mobility $\mu$ (top), brush monomer density $\rho_b$ (middle), and ion density $\rho_c$ (bottom) profiles as a function of distance $z$ to the substrate for brushes with grafting density $\Gamma = 0.01\sigma^{-2}$.

Even though the brush conformation and ion distribution depend on the manner in which $\xi$ is tuned, the resulting ion mobilities are very similar (Figure S4a,b, middle panels), showing the same strong decrease with increasing $\xi$. As Manning condensation increases, more ions migrate into the brush and ion–polymer binding is enhanced. However, the overall ion flux $\Phi$ is vastly
different in the two scenarios. An increase in Bjerrum length reduces the flux proportionally to the mobility, but an increase in polymer charge implies a growth in the number of counterions that outweighs the reduction in mobility (Figure S4a,b, bottom panels). Indeed, this is reflected in the experimentally well-established enhancement of conductivity in PEB-functionalized nanochannels.
upon protonation of the polyelectrolytes.\textsuperscript{7,8}

In this work, we have focused on salt-free systems with short polymers. When the amount of charge in the system is increased, either by introducing longer polymers or by addition of salt, both the balance between electrostatic ion binding and steric effects that governs ion conduction and the magnitude of dielectric effects will be altered by the increased electrostatic screening. However, the mechanisms observed will remain valid. We anticipate them to be particularly relevant for nanofluidic devices where interfacial phenomena are enhanced by the large surface-to-volume ratio and where precise control over ionic mobilities becomes increasingly important.

The simulations presented ignore hydrodynamic effects beyond the Langevin thermostat. Such effects are expected to be less important in dilute conditions. In fact, previous simulations of simple electrolytes\textsuperscript{9} have shown that even at 1.0 M KCl, hydrodynamic effects enhance the diffusion coefficient of $K^+$ only by $\sim3\%$. As this concentration approximately corresponds to a brush with higher grafting density than what was studied here, we don’t expect hydrodynamic interactions to drastically alter the ionic velocities in the hopping process.

In addition, the coarse-grained model lacks a description of the molecular structure of the solvent, and thus does not capture effects such as the formation of an enhanced hydrogen-bonding network for water within PEBs\textsuperscript{10} or the emergence of an oriented hydration layer at the solid–fluid interface.\textsuperscript{11} These phenomena would slow down ion transport due to hindered water diffusion and the presence of an oriented hydration layer can alter the dielectric mismatch at the interface.\textsuperscript{12,13} A detailed study of these aspects will require models with explicit water. Despite the simplifications in the current model, we consider the mechanisms uncovered here as fundamental to understanding ion transport in media where one of the charged components is immobilized and where the structure and interactions are modulated by a polarizable interface.
References


