Supplemental Information:
Transport mechanisms underlying ionic conductivity in nanoparticle-based single-ion electrolytes

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S1 Coarse-grained simulations for the region between two nanoparticles

S1.1 Simulation Details

We model the region between two functionalized nanoparticles as a fluid of oligomers and cations confined between two flat surfaces grafted with linear polymer chains and anions. The polymers each consist of 18 monomers of diameter $\sigma$ (e.g., $\sigma \approx 4.3$ Å for an ethylene oxide (EO) monomer$^1$), while the oligomers comprise 5 identically sized monomers of diameter $\sigma$. 
The simulation cell is a cuboid with length $L_z$ in the direction perpendicular to the surfaces and length $L = 13.46 \sigma$ in the two (periodically replicated) directions parallel to the flat surfaces. Based on the experimental study by Schaefer et al., we fix the grafting density of anions to be equal to that of the polymer chains ($0.0993$ per $\sigma^2$); i.e., 18 polymer chains and 18 anions per surface. This polymer grafting density corresponds to $\approx 0.42$ times the experimentally reported grafting density (190 poly(ethylene glycol) chains on 7 nm silica nanoparticle).

To maintain charge neutrality, the number of cations in the cell is equal to the number of anions (i.e., 36 ion pairs total). The number of oligomeric solvent chains in the system is varied depending on $L_z$ and the anion size, while the number of every other component in the system was fixed. When solvent chains are present, their number density is chosen to maintain a system volume fraction of 0.444 (Table S1). Such a value is equivalent to that of a fluid of monomers with number density of $0.85 \sigma^{-3}$. Below a critical value of $L_z$, no solvent is present, and the system volume fraction monotonically increases with increasing confinement due to the presence of tethered polymer chains and anions.

Table S1: Number of oligomeric solvent chains for different $L_z$ and the corresponding volume fraction and number density of the system ($\sigma_{\text{anion}} = 2.0 \sigma$).

| $L_z$ ($\sigma$) | Number of solvent chains | System volume fraction | System number density ($\sigma^{-3}$) |
|-----------------|--------------------------|------------------------|-------------------------------------|
| 15              | 260                      | 0.444                  | 0.756                               |
| 8               | 45                       | 0.444                  | 0.675                               |
| 7               | 14                       | 0.444                  | 0.651                               |
| 6.5             | 0                        | 0.448                  | 0.642                               |
| 6.0             | 0                        | 0.485                  | 0.695                               |
| 5.5             | 0                        | 0.529                  | 0.759                               |
| 5.0             | 0                        | 0.5822                 | 0.834                               |

Simulation cells are constructed by localizing the graft beads of diameter $\sigma$ for the polymer chains and anions onto each flat surface. The graft beads are evenly distributed on the surface by minimizing the total interaction energy among the grafting sites, their locations determined by assuming that they interact with each other through a purely repulsive $1/r^2$
pair potential. Every graft bead is assumed to be charge neutral with no embedded dipoles. The forces on the graft beads are fixed to be zero throughout the simulations to replicate nanoparticle-tethered polymer chains and anions. The graft beads are each bonded to a freely moving charge neutral bead with diameter $\sigma$ with no dipole moment.\textsuperscript{2} The charge neutral beads are then bonded to either the first bead of a polymer chain or an anion such that a uniform distribution of both polymer chains and anions is maintained across the flat surface. The polymer chains are randomly grown from the first bead attached to the charge neutral bead. Subsequently, the oligomeric solvent chains were grown randomly and dispersed throughout the simulation cell.

The simulations are executed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.\textsuperscript{3} All systems are initially energy minimized using the steepest descent algorithm followed by the conjugate gradient algorithm to remove heavy overlaps. Short runs are then performed in the microcanonical (NVE-limit) ensemble during which the beads are restricted from moving more than 0.1 $\sigma$ for 100 $\tau$, where $\tau = \sqrt{\sigma^2 m/\epsilon}$, $m$ is the monomer bead mass (assumed equal for all beads), and $\epsilon$ is the strength of the monomer-monomer Lennard-Jones (LJ) attraction for the polymer described in Sec. S1.2 ($\epsilon \approx 5.603 \times 10^{-21}$ J).\textsuperscript{1} This effectively removes softer particle overlaps and further relaxes the system. All simulations are subsequently equilibrated in the canonical (NVT) ensemble for another $2 \times 10^4 \tau$. Production runs for systems with $L_z \geq L_z^{\text{surface}}$ and $L_z < L_z^{\text{surface}}$ (defined in Section S4.1) are carried out via canonical ensemble simulations for a further $1.4 \times 10^5 \tau$ and $10^6 \tau$, respectively.

The time step size for all dynamics (NVE-limit, NVT) is 0.005 $\tau$. The temperature for all constant-temperature runs is $T = 373$ K.\textsuperscript{2} All thermostating is carried out with the Nosé-Hoover thermostat and explicitly accounted for the monomeric rotational degrees of freedom.\textsuperscript{4,5}
S1.2 Force Field Details

Most of the interaction potentials and the corresponding force field parameters are adapted from a previous study in our group on Stockmayer polymer electrolytes. All beads interact through a repulsive Lennard-Jones potential $E_{LJ}$:

$$E_{LJ}(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right], \quad r_{ij} \leq 2^{1/6}\sigma_{ij}, \quad (1)$$

where $r_{ij}$ is the distance between the centers of two beads $i$ and $j$. $\sigma_{ij}$ is the arithmetic mean of the bead diameters, $\sigma_i$ and $\sigma_j$, determined as $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

Further, the interaction of the beads with the nanoparticle is accounted through a repulsive LJ potential $E_{wall}$:

$$E_{wall}(r) = 4\varepsilon \left[ \left( \frac{\sigma_i}{2r} \right)^{12} - \left( \frac{\sigma_i}{2r} \right)^{6} \right], \quad r \leq 2^{1/6}\sigma_i \quad (2)$$

where $r$ is the distance between the center of the bead $i$ and the nearest wall (nanoparticle surface), and $\sigma_i$ is the diameter of the bead $i$.

All components bonded to each other (monomer-monomer, graft bead-charge neutral bead, charge neutral bead-anion, charge neutral bead-monomer) interact through the finitely extensible nonlinear elastic (FENE) potential:

$$E_{FENE}(r_{ij}) = \frac{1}{2} k R_0^2 \ln \left[ 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right] \quad (3)$$

We use the spring constant $k = 30 \varepsilon/\sigma^2$ and cutoff radius $R_0 = 1.5 \times (\sigma_i + \sigma_j)/2$.\textsuperscript{7}

In addition to the LJ potential, ions interact through the Coulomb potential $E_{zz}$:

$$E_{zz}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}}, \quad (4)$$

where $e$ is the fundamental proton charge, $z$ is either +1 (cations) or −1 (anions), and $\varepsilon_0$ is
the permittivity of free space.

Freely rotating point dipoles of constant strength are embedded in all monomers. The
strength of the dipole moment in each monomer \( i \) (\( \mu_i \)) was fixed to represent the dipole
moment of an EO monomer at 373 K (1.7 Debye), calculated by Wheatle et al.\(^6\) using
atomistic simulations. Ions and dipoles interact through the following potential:

\[
E_{qq}(r_{ij}) = \frac{e z_i}{4 \pi \varepsilon_0 r_{ij}^3} (\mu_i \cdot \mathbf{r}_{ij})
\]  

(5)

Further, dipoles embedded in monomer beads interact through the following potential:

\[
E_{\mu_i\mu_j}(r_{ij}) = \frac{1}{4 \pi \varepsilon_0} \left[ \frac{1}{r_{ij}^3} (\mu_i \cdot \mu_j) - \frac{3}{r_{ij}^5} (\mu_i \cdot \mathbf{r}_{ij})(\mu_j \cdot \mathbf{r}_{ij}) \right] x_{ij},
\]

(6)

where \( x_{ij} \) is zero if the the monomers are directly bonded and unity otherwise.

In addition to the translational degrees of freedom, the presence of freely rotating dipoles
in the monomers necessitates accounting for the associated rotational degrees of freedom and
torques on the monomers. The monomers were simulated as finite-size particles with inertia
of rotation \( I = 0.025 \text{ m} \sigma^2 \).\(^8\) Sources of torque \( T \) on the monomer beads include ion-dipole
interactions:

\[
T_{ij} = \frac{1}{4 \pi \varepsilon_0} \frac{e z_j}{r_{ij}^3} (\mu_i \times \mathbf{r}_{ij}),
\]

(7)

and dipole-dipole interactions:

\[
T_{ij} = \frac{1}{4 \pi \varepsilon_0} \left[ -\frac{1}{r_{ij}^3} (\mu_i \times \mu_j) + \frac{3}{r_{ij}^5} (\mu_j \cdot \mathbf{r}_{ij})(\mu_i \times \mathbf{r}_{ij}) \right]
\]

(8)
S2 Simulations to generate multiparticle configurations

S2.1 Model

We consider a system of identical model nanoparticles in a cubic box of fixed length \( l \) with periodic boundary conditions. The number of nanoparticles \( N \) is varied to generate a volume fraction \( \phi = N \pi \sigma_{\text{NP}}^3 / 6l^3 \), where \( \sigma_{\text{NP}} \) represents the diameter of a bare nanoparticle. To mimic the disparity between the experimentally reported silica nanoparticle size (7 nm)\(^2\) and that of an EO monomer (4.3 Å),\(^1\) the nanoparticles are represented as larger spheres with \( \sigma_{\text{NP}} = 16.2 \sigma \). Assuming the density of the nanoparticle to be equal to that of an EO monomer, the mass of the nanoparticle is fixed to be \( m_{\text{NP}} = 4251.53 \text{ m} \). The box size is chosen to be \( l = 162 \sigma \). Representative nanoparticle configurations are generated from equilibrium simulations using the pair potential, \( U(r) \), calculated based on the interactions between two functionalized silica nanoparticles. To that end, we assume the contributions to the effective pair potential from the bare nanoparticles and the functionalizing components, respectively, to be additive,

\[
U(r) = U_{\text{bare}}(r) + U_{\text{func}}(r),
\]

(9)

where \( U_{\text{bare}}(r) \) is the pair interaction between bare silica nanoparticles and \( U_{\text{func}}(r) \) is the effective pair interaction between non-interacting nanoparticles due to the solvent and the components functionalized on the nanoparticle surfaces.

A semiempirical pair potential proposed by Lee and Hua\(^9\) is considered to represent the pair interactions of coarse-grained (bare) silica nanoparticles,

\[
U_{\text{bare}}(r) = \begin{cases} 
4 \epsilon_{\text{bare}} \left[ \left( \frac{\sigma_{\text{NP}}}{r} \right)^{2\alpha} - \left( \frac{\sigma_{\text{NP}}}{r} \right)^{\alpha} \right], & r \leq 1.71\sigma_{\text{NP}} \\
0, & r \geq 1.71\sigma_{\text{NP}},
\end{cases}
\]

(10)

where \( \epsilon_{\text{bare}} \) and \( \alpha \) are nanoparticle size-dependent parameters.\(^9,10\) Considering the nanoparticle size reported in the experimental study and the parametrization in our study, these
parameters are calculated to be $\epsilon_{\text{bare}} = 40.84 \epsilon$ and $\alpha = 33.9$.

We calculate the potential of mean force (PMF) between two non-interacting particles as a function of their distance to quantify the contribution of functionalized components (including solvent) to the effective pair potential between particles. Explicitly, we approximate the force between the spherical particles, $F(r)$, based on the Derjaguin approximation for two spheres of equal radii $R$,

$$F(r) = 2\pi R W(D)_{\text{planes}},$$  

(11)

where $W(D)_{\text{planes}}$ is the interaction energy per unit area of the two functionalized planar surfaces at a separation distance $D$. The pair potential due to the functionalized components, $U_{\text{func}}(r)$, is expressed in terms of the mean force as

$$U_{\text{func}}(r) = \int_r^\infty dr' F(r')$$  

(12)

**S2.2 Simulation Methodology**

We perform molecular dynamics (MD) simulations to obtain the equilibrium configurations of nanoparticles using the LAMMPS\textsuperscript{3} package. To carry out such simulations, we start from a random initial configuration of particles and equilibrate the system for $5 \times 10^8$ steps in the canonical ensemble with time step $dt = 0.001\sqrt{\sigma^2 m / \epsilon}$. The temperature considered is $T = 373$ K.\textsuperscript{2} Temperature is maintained using a Nosé-Hoover thermostat.\textsuperscript{4,5}
S3 Simulations for the ionic conductivity

On-lattice kinetic Monte Carlo (kMC) simulations are based on a master equation\textsuperscript{12} in which the probability distribution $P(\omega_i, t)$ for being in state $\omega_i$ at time $t$ evolves as follows:

$$\frac{dP(\omega_i, t)}{dt} = \sum_{j \neq i} k_{ji} P(\omega_j, t) - \sum_{i \neq j} k_{ij} P(\omega_i, t), \quad (13)$$

where $k_{ij}$ is the transition (hopping) rate from state $\omega_i$ to $\omega_j$. In the context of our system, the lattice sites with different transition rates or different affinities to host a cation are labeled with unique states. A transition or a move corresponds to the hop of a cation to a neighboring site (in the $\pm x, \pm y, \pm z$ direction). In this work, we implemented the direct kMC method,\textsuperscript{13–15} one of the widely used rejection-free algorithms to solve the master equation (Eq. 13).

Figure S1: Distribution of anions near the surface for the case: $\sigma_{\text{cat}} = 0.5 \, \sigma$, $\mu = \mu_{\text{EO}}$. The dashed and solid lines represents the case with $\sigma_{\text{anion}} = 2.0 \, \sigma$ and $1.5 \, \sigma$, respectively. The anion distribution for different $L_z$ values are denoted with red ($L_z = 15.0 \, \sigma$) and blue ($L_z = 8.0 \, \sigma$) lines.

Based on the analysis of lattice spacing effects in kMC simulations (Section S5.2), we choose a lattice spacing of 0.32 $\sigma$. We first map the nanoparticle centers onto the lattice sites. With these sites as center, we then assume the sites within a sphere of radius 0.5 $\sigma_{\text{NP}}$ to be occupied by the nanoparticles. The simulation cell consists of 1024 noninteracting tracer
cations placed randomly on sites not occupied by the particle. We note that a large number of tracer cations are present in order to increase sampling in the estimation of the cation self-diffusion coefficient (i.e., their concentration in the simulation is not reflective of a physical concentration of cations in the system). For our system, the nanoparticles are the only source of cations. Hence, \( N_{\text{cat}} \) is proportional to the particle volume fraction. Based on the choice of coarse-grained parameters in our study, we assume \( N_{\text{cat}} = 80 \times N \), to appropriately map the number of Li\(^+\) for every particle as reported in the experimental system.\(^2\) Every kMC simulation run lasted for \( 3 \times 10^6 \) moves. From the resulting trajectories of the tracers, we extract the mobility of the cations using the Einstein-Smoluchowski relation:

\[
D_{\text{cat}} = \lim_{t \to \infty} \frac{1}{6t} \langle (r(t) - r(0))^2 \rangle, \tag{14}
\]

where \( \langle (r(t) - r(0))^2 \rangle \) is the mean squared displacement (MSD) of cations at time \( t \). The \( D_{\text{cat}} \) values reported in this study are averaged over 30 independent kMC simulations for each system.

**S4 Details of analysis**

**S4.1 Calculating \( D_{\parallel} \) in the non-overlapping surface region**

For the coarse-grained simulations modeling the region between two nanoparticles, positions that lie a distance \( z \) to the closest nanoparticle surface, where \( 0 \leq z \leq L_z^{\text{surface}} \), are denoted part of the “surface” region. Accordingly, the surface region was identified to be “non-overlapping” for the cases with \( L_z > 2 \ L_z^{\text{surface}} \). The \( L_z^{\text{surface}} \) value was chosen to represent the maximum distance from the surface at which the cations could interact strongly with the anions. Based on the distribution of anions (Figure S1), the \( L_z^{\text{surface}} \) value chosen to be 3.5 \( \sigma \) and 3.0 \( \sigma \) for the cases with \( \sigma_{\text{anion}} = 2.0 \ \sigma \) and 1.5 \( \sigma \), respectively.

Using the methodology introduced by Berne and coworkers,\(^{16}\) we calculate the local
Figure S2: Results for cation dynamics in the non-overlapping surface region for the cases with (a) different anion sizes ($\sigma_{\text{cat}} = 0.5 \sigma$, $\mu = \mu_{\text{EO}}$), (b) different cation sizes at low polarity ($\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = \mu_{\text{EO}}$), and (c) different cation sizes at high polarity ($\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$). The solid ($L_z = 15 \sigma$) and dashed ($L_z = 8 \sigma$) lines represent different separation distances between the nanoparticles.

cation diffusivity:

\[
D_{\parallel} = \lim_{t \to \infty} \frac{\langle (r_{\parallel}(t) - r_{\parallel}(0))^2 \rangle_{\text{surface}}}{4t P(t)}, \tag{15}
\]

where $\langle (r_{\parallel}(t) - r_{\parallel}(0))^2 \rangle_{\text{surface}}$ is the mean squared displacement (MSD) of cations in the directions parallel to the surface in the region, $0 \leq z \leq L_{z \text{surface}}$, at time $t$. The survival probability of cations $P(t)$ denotes the averaged probability for the cations to remain in the surface region at time $t$. Figure S2 shows the cation dynamics in the non-overlapping surface region for all the cases considered in this study.

S4.2 Calculating $D_{\parallel}$ in the overlapping surface region

For the cases with $L_z < 2 L_{z \text{surface}}$, the surface regions associated with both the nanoparticles merge. In this scenario, the cation transport through the entire region is in the vicinity of anions. Hence, the local cation diffusivity is assumed to be uniform throughout the region between the two surfaces, and is calculated using the Einstein-Smoluchoski relation:

\[
D_{\parallel} = \lim_{t \to \infty} \frac{1}{4t} \langle (r_{\parallel}(t) - r_{\parallel}(0))^2 \rangle \tag{16}
\]

As shown in Figure S3, the cations reach the diffusive regime for all the cases.
Figure S3: Cation MSDs in the overlapping surface region for different ion sizes and polarities. Different colors correspond to different $L_z$ values.
S4.3 Calculating $D_{\parallel}$ in the bulk region

![Graphs showing distribution of cations in the bulk region](image)

Figure S4: Distribution of cations in the bulk region (in the presence of the external biased potential) for (a) low polarity case with $\epsilon_{bias} = 2\epsilon$ and (b) high polarity case with $\epsilon_{bias} = 0.25\epsilon$. Different colors correspond to different cation sizes.

We denote the region occupied by the solvent molecules as “bulk”, and we assume that the cation diffusivity in this region is independent of the $L_z$ value and the anion size. To that end, we calculate the $D_{\parallel}$ value in the bulk region for a system with large separation distance between the two flat surfaces ($L_z = 30\sigma$). For the low polarity case, due to the negligible cation presence in the bulk region, the methodology employed to calculate the local cation diffusivity in Section S4.1 cannot be extended to extract the local cation diffusivity in the bulk region. For the high polarity case, the local diffusivities in the bulk region, calculated using the similar methodology, were inconclusive due to the faster movement of cations in the bulk region resulting in considerable statistical noise. Alternatively, to facilitate the cation presence in the bulk region, the cations were initialized within the region, $7\sigma \leq z \leq 23\sigma$, where $z$ in this context denotes the distance from either surface. The cations were restricted to move outside this region throughout the dynamics. Additionally, to maintain a uniform distribution of cations throughout this region, an external biasing potential is applied on the cations. Explicitly, in addition to its interaction with the solvent chains, the cations experience an additional harmonic spring potential $E_{bias}$:
\[ E_{bias}(z) = \begin{cases} 
\epsilon_{bias}(z - 11\sigma)^2, & 7\sigma \leq z \leq 11\sigma \\
0, & 11\sigma < z < 19\sigma \\
\epsilon_{bias}(z - 19\sigma)^2, & 19\sigma \leq z \leq 23\sigma, 
\end{cases} \]

where \( \epsilon_{bias} = 2\epsilon \) and \( 0.25\epsilon \) for the low and high polarity cases, respectively. The above parameters were chosen to ensure uniform distribution of cations throughout the bulk region, as shown in Figure S4.

Restricting the movement of cations in the bulk region allowed for calculating reliable \( D_\parallel \) values (using Eq. 16). The cation MSDs in the bulk region are shown in Figure S5.

Figure S5: Cation MSDs in the bulk region for (a) low polarity case and (b) high polarity case. Different colors correspond to different cation sizes.

### S4.4 Assigning transition rates in the on-lattice kMC model

Lattice sites with similar local diffusivities and affinities to host a cation are denoted as unique states \( \omega_i \) (as defined in Eq. 13) for cations (tracers). To that end, the sites occupied by the nanoparticles are denoted as state \( \omega_0 \). Based on the distribution of cations and local cation diffusivities in the MD simulations, we define six unique states \( (\omega_i, i = 1,\ldots,6) \) for the tracers to be present on the sites not occupied by nanoparticles (Figure S6).

Explicitly, sites belonging to states \( \omega_1, \omega_2 \) and \( \omega_3 \) represent the “surface” sites. Sites
Figure S6: Representation of the different states defined for lattice sites with unique hopping rates or affinities to host a cation. (a) Large interparticle separation with no influence of the neighboring particle. (b) Relatively smaller interparticle separation with influence of neighboring particle on the cation dynamics in the bulk region between particles. (c) Significantly close particles resulting in altered cation dynamics in the overlapping surface region.

belonging to each of these three states host cations with equal affinities, but offer different local diffusivities. Based on the local diffusivities in the surface region for different $L_z$ values (Figures 2c, 3b and 4c in the main text), the sites corresponding to the non-overlapping surface region are assigned to state $\omega_1$, with the transition rates being equal to the local diffusivities in this region. Similarly, the sites corresponding to the overlapping surface region with unique local diffusivities are assigned to states $\omega_2$ and $\omega_3$ as shown in Figure S6(c). The “bulk” sites were represented by sites corresponding to the remaining states ($\omega_4$, $\omega_5$ and $\omega_6$). In contrast to the states representing the surface sites, the different states representing the bulk region offer similar local diffusivities but exhibit different affinities to host a cation. Precisely, to capture the non-uniform cation distribution in the bulk region, observed for
Figure S7: Cation distribution in the region between two flat surfaces for different ion sizes and polarities. Different colors correspond to different $L_z$ values.
the cases with $L_z = 15 \sigma$ (Figure S7), we define two sub-regions in the bulk region denoted by states $\omega_4$ and $\omega_6$. Further, for the case with relatively smaller separations, the cation presence in the bulk region between the nanoparticles is slightly enhanced (Figure S7) due to the relatively stronger electrostatic interactions with the anions tethered to either surface. Hence, we define a unique state $\omega_5$ as illustrated in Figures S6(b) and S6(c) representing the sites corresponding to the bulk region between two nanoparticles with relatively smaller separation distance.

In Tables S2-S12, we provide details on: (a) the conditions to be satisfied by each lattice site to be associated with a particular state; and (b) transition rate ($k_{ii}$) and (c) the relative affinity of sites to host a cation compared to sites with state $\omega_1$, $P(\omega_i, eq)/P(\omega_1, eq)$. We denote the shortest distance between a lattice site and the surface of the nearest nanoparticle as $r_1$, and that between a lattice site and the surface of the second nearest nanoparticle as $r_2$.

Table S2: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.5 \sigma$, $\sigma_{\text{anion}} = 1.5 \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|-------------------------------|----------------------------------|
| 1          | $r_1 < 3.25 \sigma$ OR $6 \sigma < (r_1 + r_2) < 6.5 \sigma$ | 0.000054                     | 1                               |
| 2          | $5.5 \sigma < (r_1 + r_2) < 6 \sigma$            | 0.000054                     | 1                               |
| 3          | $(r_1 + r_2) < 5.5 \sigma$                       | 0.00000644                   | 1                               |
| 4          | $3.25 \sigma < r_1 < 3.6 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.033                       | $2.22 \times 10^{-4}$           |
| 5          | $r_1 > 3.25 \sigma$ AND $6.4 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.033                       | $4.6 \times 10^{-4}$           |
| 6          | $r_1 > 3.6 \sigma$                                | 0.033                       | $4.0 \times 10^{-6}$           |

Table S3: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.25 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|-------------------------------|----------------------------------|
| 1          | $r_1 < 3.5 \sigma$ OR $6 \sigma < (r_1 + r_2) < 7 \sigma$ | 0.00256                     | 1                               |
| 2          | $5 \sigma < (r_1 + r_2) < 6 \sigma$            | 0.0006197                    | 1                               |
| 3          | $(r_1 + r_2) < 5 \sigma$                       | 0.000338                     | 1                               |
| 4          | $3.5 \sigma < r_1 < 4.9 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.03235                     | 0.015                           |
| 5          | $r_1 > 3.5 \sigma$ AND $7 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.03235                     | 0.0672                          |
| 6          | $r_1 > 4.9 \sigma$                                | 0.03235                     | $5.5 \times 10^{-4}$          |
Table S4: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.5 \, \sigma$, $\sigma_{\text{anion}} = 2.0 \, \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} \,(\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|--------------------------------------------------|------------------|---------------------------------|
| 1          | $r_1 < 3.5 \, \sigma$ OR $6 \, \sigma < (r_1 + r_2) < 7 \, \sigma$ | 0.003           | 1                               |
| 2          | $5 \, \sigma < (r_1 + r_2) < 6 \, \sigma$ | 0.00069         | 1                               |
| 3          | $(r_1 + r_2) < 5 \, \sigma$ | 0.00030         | 1                               |
| 4          | $3.5 \, \sigma < r_1 < 4.9 \, \sigma$ AND $(r_1 + r_2) > 8 \, \sigma$ | 0.033           | 0.0095                          |
| 5          | $r_1 > 3.5 \, \sigma$ AND $7 \, \sigma < (r_1 + r_2) < 8 \, \sigma$ | 0.033           | 0.0426                          |
| 6          | $r_1 > 4.9 \, \sigma$ | 0.033           | $6.06 \times 10^{-4}$          |

Table S5: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.75 \, \sigma$, $\sigma_{\text{anion}} = 2.0 \, \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} \,(\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|--------------------------------------------------|------------------|---------------------------------|
| 1          | $r_1 < 3.5 \, \sigma$ OR $6 \, \sigma < (r_1 + r_2) < 7 \, \sigma$ | 0.00361         | 1                               |
| 2          | $5 \, \sigma < (r_1 + r_2) < 6 \, \sigma$ | 0.000425        | 1                               |
| 3          | $(r_1 + r_2) < 5 \, \sigma$ | 0.000082        | 1                               |
| 4          | $3.5 \, \sigma < r_1 < 4.9 \, \sigma$ AND $(r_1 + r_2) > 8 \, \sigma$ | 0.04719         | 0.0085                          |
| 5          | $r_1 > 3.5 \, \sigma$ AND $7 \, \sigma < (r_1 + r_2) < 8 \, \sigma$ | 0.04719         | 0.0247                          |
| 6          | $r_1 > 4.9 \, \sigma$ | 0.04719         | $3.854 \times 10^{-4}$         |

Table S6: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.85 \, \sigma$, $\sigma_{\text{anion}} = 2.0 \, \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} \,(\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|--------------------------------------------------|------------------|---------------------------------|
| 1          | $r_1 < 3.5 \, \sigma$ OR $6 \, \sigma < (r_1 + r_2) < 7 \, \sigma$ | 0.00267         | 1                               |
| 2          | $5 \, \sigma < (r_1 + r_2) < 6 \, \sigma$ | 0.000141        | 1                               |
| 3          | $(r_1 + r_2) < 5 \, \sigma$ | 0.0000078       | 1                               |
| 4          | $3.5 \, \sigma < r_1 < 4.9 \, \sigma$ AND $(r_1 + r_2) > 8 \, \sigma$ | 0.0404          | 0.00849                         |
| 5          | $r_1 > 3.5 \, \sigma$ AND $7 \, \sigma < (r_1 + r_2) < 8 \, \sigma$ | 0.0404          | 0.0293                          |
| 6          | $r_1 > 4.9 \, \sigma$ | 0.0404          | $3.833 \times 10^{-4}$         |

Table S7: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 1.0 \, \sigma$, $\sigma_{\text{anion}} = 2.0 \, \sigma$, $\mu = \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} \,(\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|--------------------------------------------------|------------------|---------------------------------|
| 1          | $r_1 < 3.5 \, \sigma$ OR $6 \, \sigma < (r_1 + r_2) < 7 \, \sigma$ | 0.0021           | 1                               |
| 2          | $5 \, \sigma < (r_1 + r_2) < 6 \, \sigma$ | 0.0000494       | 1                               |
| 3          | $(r_1 + r_2) < 5 \, \sigma$ | 0.000002        | 1                               |
| 4          | $3.5 \, \sigma < r_1 < 4.9 \, \sigma$ AND $(r_1 + r_2) > 8 \, \sigma$ | 0.03678         | 0.0112                          |
| 5          | $r_1 > 3.5 \, \sigma$ AND $7 \, \sigma < (r_1 + r_2) < 8 \, \sigma$ | 0.03678         | 0.0274                          |
| 6          | $r_1 > 4.9 \, \sigma$ | 0.03678         | $4.49 \times 10^{-4}$          |
Table S8: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.25 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|----------------------|-------------------------------|
| 1          | $r_1 < 3.5 \sigma$ OR $6 \sigma < (r_1 + r_2) < 7 \sigma$ | 0.00014             | 1                             |
| 2          | $5 \sigma < (r_1 + r_2) < 6 \sigma$              | 0.0000661           | 1                             |
| 3          | $(r_1 + r_2) < 5 \sigma$                         | 0.000119            | 1                             |
| 4          | $3.5 \sigma < r_1 < 4.9 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.02404             | 0.279                         |
| 5          | $r_1 > 3.5 \sigma$ AND $7 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.02404             | 0.677                         |
| 6          | $r_1 > 4.9 \sigma$                               | 0.02404             | 0.398                         |

Table S9: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.5 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|----------------------|-------------------------------|
| 1          | $r_1 < 3.5 \sigma$ OR $6 \sigma < (r_1 + r_2) < 7 \sigma$ | 0.00053             | 1                             |
| 2          | $5 \sigma < (r_1 + r_2) < 6 \sigma$              | 0.00013              | 1                             |
| 3          | $(r_1 + r_2) < 5 \sigma$                         | 0.00002              | 1                             |
| 4          | $3.5 \sigma < r_1 < 4.9 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.0325              | 0.278                         |
| 5          | $r_1 > 3.5 \sigma$ AND $7 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.0325              | 0.59                          |
| 6          | $r_1 > 4.9 \sigma$                               | 0.0325              | 0.318                         |

Table S10: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.75 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|----------------------|-------------------------------|
| 1          | $r_1 < 3.5 \sigma$ OR $6 \sigma < (r_1 + r_2) < 7 \sigma$ | 0.00174             | 1                             |
| 2          | $5 \sigma < (r_1 + r_2) < 6 \sigma$              | 0.000277            | 1                             |
| 3          | $(r_1 + r_2) < 5 \sigma$                         | 0.000118            | 1                             |
| 4          | $3.5 \sigma < r_1 < 4.9 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.04289             | 0.368                         |
| 5          | $r_1 > 3.5 \sigma$ AND $7 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.04289             | 0.92                          |
| 6          | $r_1 > 4.9 \sigma$                               | 0.04289             | 0.737                         |

Table S11: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 0.85 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii} (\sigma^2 \tau^{-1})$ | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|------------|-------------------------------------------------|----------------------|-------------------------------|
| 1          | $r_1 < 3.5 \sigma$ OR $6 \sigma < (r_1 + r_2) < 7 \sigma$ | 0.0022              | 1                             |
| 2          | $5 \sigma < (r_1 + r_2) < 6 \sigma$              | 0.000782            | 1                             |
| 3          | $(r_1 + r_2) < 5 \sigma$                         | 0.000097            | 1                             |
| 4          | $3.5 \sigma < r_1 < 4.9 \sigma$ AND $(r_1 + r_2) > 8 \sigma$ | 0.05317             | 0.399                         |
| 5          | $r_1 > 3.5 \sigma$ AND $7 \sigma < (r_1 + r_2) < 8 \sigma$ | 0.05317             | 1.012                         |
| 6          | $r_1 > 4.9 \sigma$                               | 0.05317             | 0.638                         |
Table S12: Inputs to kMC model for the case: $\sigma_{\text{cat}} = 1.0\, \sigma$, $\sigma_{\text{anion}} = 2.0\, \sigma$, $\mu = 2\, \mu_{\text{EO}}$

| $\omega_i$ | Conditions satisfied by the lattice sites corresponding to $\omega_i$ | $k_{ii}$ ($\sigma^2\tau^{-1}$) | $P(\omega_i, eq)/P(\omega_1, eq)$ |
|---|---|---|---|
| 1 | $r_1 < 3.5\, \sigma$ OR $6\, \sigma < (r_1 + r_2) < 7\, \sigma$ | 0.0045 | 1 |
| 2 | $5\, \sigma < (r_1 + r_2) < 6\, \sigma$ | 0.00063 | 1 |
| 3 | $(r_1 + r_2) < 5\, \sigma$ | 0.0000268 | 1 |
| 4 | $3.5\, \sigma < r_1 < 4.9\, \sigma$ AND $(r_1 + r_2) > 8\, \sigma$ | 0.05694 | 0.4389 |
| 5 | $r_1 > 3.5\, \sigma$ AND $7\, \sigma < (r_1 + r_2) < 8\, \sigma$ | 0.05694 | 1.194 |
| 6 | $r_1 > 4.9\, \sigma$ | 0.05694 | 0.755 |

Based on the detailed balance criterion at thermodynamic equilibrium for the master equation (Eq. 13), the following condition for transition rates from state $\omega_i$ to $\omega_j$ was imposed:

$$ k_{ij} P(\omega_i, eq) = k_{ji} P(\omega_j, eq) \quad (18) $$

For the case $i \neq j$, if $P(\omega_i, eq) < P(\omega_j, eq)$, we choose the value of $k_{ji}$ to be equal to $k_{jj}$. The value of $k_{ij}$ is then fixed based on the condition in Eq. 18.

**S5 Supporting Results**

**S5.1 Effective pair potential and nanoparticle morphologies**

The results for the effective pair potential, $U(r)$, between the functionalized nanoparticles are presented in Figure S8(a). We observe that the effective interaction between nanoparticles is repulsive for all separation distances due to the dominant contribution from the functionalized components ($U_{\text{func}}(r)$) to the effective pair potential. From the resulting equilibrium morphologies at different nanoparticle volume fractions, we quantify the proximity between neighboring nanoparticles. To that end, we denote $\overline{d}$ to be the shortest distance between the surface of a particle and the surface of its nearest neighbor, averaged over all particles. From the results reported in Figure S8(b), it is evident that at low volume fractions, the nanoparticles are distant from each other due to the repulsive interactions between the nanoparticles (Figure S8(a)). The $\overline{d}$ values are seen to decrease with increasing nanoparticle loading.
Figure S8: (a) Effective pair interactions between functionalized nanoparticles along with the contribution of individual components. (b) Shortest distance between the surfaces of a particle and its nearest neighbor, averaged over all particles, at different nanoparticle loadings.

S5.2 Effect of lattice spacing in kMC simulations

Figure S9: Effect of lattice spacing $a$ on diffusivity $D_{\text{cat}}$ for the cases: (a) $\sigma_{\text{cat}} = 0.5 \sigma$, $\sigma_{\text{anion}} = 1.5 \sigma$, $\mu = \mu_{\text{EO}}$, (b) $\sigma_{\text{cat}} = 0.5 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = \mu_{\text{EO}}$, and (c) $\sigma_{\text{cat}} = 0.5 \sigma$, $\sigma_{\text{anion}} = 2.0 \sigma$, $\mu = 2 \mu_{\text{EO}}$.

The lattice spacing $a$ in the kMC simulations was chosen based on its effect on the $D_{\text{cat}}$ values. To test this effect, we select three cases spanning a vast range of diffusivities (Figure S9). As shown in Figure S9, for different lattice spacing values considered in this study, namely, (i) $a = 0.22 \sigma$, (ii) $a = 0.32 \sigma$, and (iii) $a = 0.43 \sigma$, the $D_{\text{cat}}$ values exhibit a qualitatively similar trend with particle volume fraction. Further, the difference between the $D_{\text{cat}}$ values with $a = 0.32 \sigma$ and $0.22 \sigma$ was less than 6% for all three cases with different regimes of diffusivities. We thus selected a lattice spacing of $0.32 \sigma$ for all the kMC
Figure S10: (a) Anion-cation radial distribution functions. (b) Average anion-cation coordination number ($\bar{n}$) in the overlapping surface region for the case: $\sigma_{\text{cat}} = 0.5 \sigma$, $\mu = \mu_{\text{EO}}$.

S5.3 Mean-squared displacement of tracer cations from kMC simulations

The cation diffusion coefficient in the multiparticle system was extracted from the slope of the long-time mean-squared displacement of tracer cations (Eq. 14). From the MSDs shown in Figure S11, it is evident that the tracers reach the diffusive regime in the kMC simulations for all the cases.

S5.4 Anion-cation coordination

To rationalize the lower cation diffusivities in the overlapping surface regions compared to those in the non-overlapping surface region for the low polarity case (Figure 2c in the main text), we characterized the ion pair electrostatic interactions in the overlapping surface regions ($L_z \leq L_z^{\text{surface}}$). To that end, we report the average anion-cation coordination number ($\bar{n}$) for two cases with different anion sizes. The cation size was fixed to be $\sigma_{\text{cat}} = 0.5 \sigma$.

The cutoff distance for anion-cation coordination was decided based on the anion-cation radial distribution function (Figure S10(a)). From the results displayed in Figure S10(b), it
Figure S11: Cation (tracer) MSDs from kMC simulations for cases corresponding to different ion sizes and polarities. Different colors correspond to different nanoparticle volume fractions.
is seen that for a fixed anion size, the $\bar{w}$ value increases with decreasing $L_z$. This suggests stronger ion pair electrostatic interactions with decreasing $L_z$ values, thus rationalizing the decreased cation mobilities in the overlapping surface region.

### S5.5 Influence of cation mobilities in the overlapping surface region

![Figure S12](image.png)

Figure S12: (a) Fraction of cations hosted by bulk (green symbols), non-overlapping (blue symbols) and overlapping (red symbols) surface sites for the case: $\sigma_{\text{cat}} = 0.5 \sigma$, $\mu = \mu_{EO}$. (b) Cation diffusivity for the fictitious case with $D_\parallel$ values in the overlapping surface region being equal to that in the non-overlapping surface region. Solid and open symbols represent results for larger and smaller anion size, respectively.

To understand the eventual decrease in the cation diffusivities at larger volume fractions (Figure 2a of the main text), we present results highlighting the contribution of the relatively slower cation transport in overlapping surface regions. In Figure S12(a), we present results for the fraction of cations hosted on different site types. Explicitly, the surface sites are categorized into non-overlapping and overlapping surface sites. It is evident that for both the cases with different anion sizes, the cation presence on the overlapping surface sites monotonically increases with particle volume fraction at higher particle loadings ($\phi > 0.25$). This results in a significant influence of the cation transport through the overlapping surface region on the overall cation diffusivities. To further support this hypothesis, we repeat our
calculations for a fictitious case with $D_\parallel$ values in the overlapping surface region being equal
to those in the non-overlapping surface region. To that end, we modify the kMC inputs
in Tables S2 and S4. Explicitly, we set $k_{22}$ and $k_{33}$ values to be equal to $k_{11}$. From the
results displayed in Figure S12(b), the eventual decrease in $D_{\text{cat}}$ values is not observed for
such a fictitious case. This indicates that the eventual decrease in $D_{\text{cat}}$ values at higher
particle volume fractions (Figure 2a of the main text) can be attributed to the slower cation
transport in the overlapping surface region.

S5.6 Distribution of cations for different cation sizes

Figure S13: (a) Fraction of cations hosted by bulk (green symbols) and surface (blue
symbols) sites for the low polarity case. (b) Fraction of cations hosted by bulk (green
symbols), non-overlapping (blue symbols) and overlapping (red symbols) surface sites for
the low polarity case. Different cation sizes are represented as $\sigma_{\text{cation}} = 0.25 \sigma$ (circle), $0.5 \sigma$
(triangle), $0.75 \sigma$ (square), $0.85 \sigma$ (diamond) and $1.0 \sigma$ (star).

Figures S13(a) and S13(b) shows the cation distribution on different site types to be
similar for all cation sizes.

S5.7 Cation-solvent association autocorrelation function

The metrics employed to understand the trend for cation diffusivities in the bulk region with
increasing cation size is the cation-solvent association autocorrelation function $C(t)$. The
The association autocorrelation function is defined as:

\[
C(t) = \frac{\langle h(t_0)h(t_0 + t) \rangle}{h}
\]  

(19)

where \( h(t) \) takes a value of one if a cation-solvent association is present at time \( t \) and zero otherwise.\(^{17} \) The autocorrelation function \( C(t) \) shows on average how long a cation-solvent pair remains associated.

\[\text{Figure S14: (a) Cation-solvent radial distribution functions. (b) Cation-solvent association autocorrelation functions for the high polarity case. Different colors correspond to different cation sizes.}\]

The cutoff distance for cation-solvent association is decided based on the cation-solvent radial distribution functions depicted in Figure S14(a). From the results displayed in Figure S14(b), it is evident that for the high polarity case \( (\mu = 2 \mu_{EO}) \), the cation-solvent association function decays faster with increasing cation size. This indicates that the increased cation diffusivity in the bulk region with increasing cation size can be understood by the movement of cations in contact with the dipolar solvent beads. For systems with highly asymmetric sizes \( (\sigma_{\text{cat}} = 0.25 \, \sigma) \), the cation strongly associates with solvent chains and cation transport by vehicular motion also seems to contribute considerably.
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