

Nonohmic Ionic Conductivity and Bulk Current Rectification in Nanoparticle Superlattices

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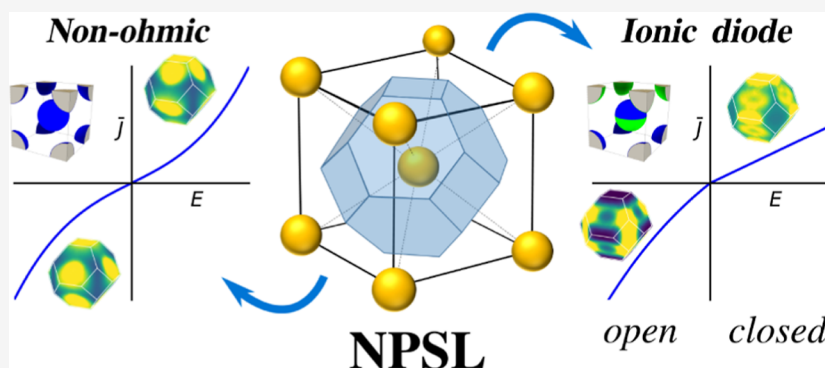
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ABSTRACT: Nanoparticle superlattices (NPSLs) are self-assembled materials formed by periodically ordered monodisperse nanoparticles (NPs). This work theoretically studies the mechanisms of ion transport in NPSLs made of polyelectrolyte-modified NPs, which are relevant in chemoelectronics and nanofluidic applications. The ion fluxes in the NPSLs are obtained by solving the three-dimensional Poisson–Nernst–Planck equations. An analytic perturbation theory is also presented to prove the generality of some of the numerical results. We consider superlattices made of charged NPs and their monovalent counterions and systematically study the effects of the lattice parameter, supercrystalline structure, and added salt on the bulk ionic conductivity of the lattice. Nonohmic current–potential responses obtained for large NP separations, low dielectric constants, and absence of added salt are explained in terms of the reorganization of the ionic concentrations in the nonequilibrium steady state. It is also shown that NPs with asymmetric charge distribution (Janus NPs) give rise to bulk current rectification. This result provides a proof of concept for the fabrication of nanofluidic and chemoelectronic elements based on NPSLs that works as the ionic equivalents of electronic diodes.

INTRODUCTION

Nanoparticle superlattices (NPSLs), self-assembled materials composed of periodically organized nanoparticles, are the mesoscopic analogues of ionic and covalent crystals.^{1–3} Over the past decade, these materials have attracted the attention of the scientific community because of their potential applications in photonics,^{4–6} plasmonics,^{5,7,8} and nanoelectronics.^{9,10} NPSLs also find applications in recently developed areas of research, such as chemoelectronics^{9,11,12} (the field devoted to the processing of chemical stimuli by logic circuits), iontronics¹³ (devices where electric currents are controlled by ion fluxes), and nanofluidics^{14–17} (which studies fluid flows at the nanoscale and nanoporous membranes). Ion transport has been previously studied in solid-state devices made of thin films of superlattices of charged NPs.^{9–12} In those systems, ion fluxes create built-in electric fields in the material, which affect their electric conductivity. Ion conduction is also relevant in single-ion electrolytes composed of charged NPs and their monovalent counterions, without added salt.^{18,19} Recently, charge- and size-selective transport,^{14,15} and ion-current rectification²⁰ have been demon-

strated for free-standing superlattices of charged NPs in contact with an electrolyte solution. NPSL membranes, therefore, share some similarities with bipolar and asymmetric nanopores, which have been extensively studied in the literature, both experimentally^{21–25} and theoretically.^{26–30} Despite those similarities, our understanding of the ionic conductivity in NPSLs is significantly less developed than that in nanopore membranes.

Based on the examples discussed above, improving our understanding of nonlinear ionic fluxes in NPSLs is a valuable research direction. In a step in that direction, Lionello et al.³¹ recently used molecular dynamics (MD) simulations to study the ionic conductivity of the citrate counterions of gold NPs

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48 coated with (11-mercaptopundecyl)-*N,N,N*-trimethylammo-
 49 nium (TMA) ligands in a fcc NPSL. This system exhibits
 50 nonohmic ionic conductivity, which is reminiscent of the
 51 nonlinear electronic conductivity of semiconductors. This
 52 nonlinear behavior was explained in terms of an insulator-to-
 53 conductor transition due to the reorganization of the citrate
 54 counterions upon increasing the electric field.³¹ Olvera de la
 55 Cruz and co-workers found a similar behavior for a binary
 56 assembly of large and small oppositely charged NPs.³² In this
 57 case, the authors also observed an insulator-to-conductor
 58 transition, as well as other complex behaviors for high electric
 59 fields, such as laning and melting of the NPSL. In both
 60 examples,^{31,32} the mobile particles contained multiple charges,
 61 which introduce very strong lattice-ion correlations. Therefore,
 62 it is intriguing to consider whether nonohmic behaviors can
 63 also occur for single-charged counterions.

64 This paper proposes a theoretical framework to study the
 65 bulk ionic conductivity of NPSLs that combines a molecular
 66 theory (MOLT)³³ to obtain the structure of the NP ligands
 67 with the Poisson–Nernst–Planck (PNP) equations^{34,35} to
 68 describe ion transport under an applied electric field. This
 69 approach is fully three-dimensional (3D) and thus explicitly
 70 considers the supercrystalline structure and orientation. In
 71 contrast, previous one-dimensional PNP models for NPSLs³⁶
 72 provided a macroscopic description of ion transport at the
 73 device level and cannot predict the nonlinear bulk conductivity
 74 described in this work. The efficiency of our 3D-PNP scheme
 75 compares favorably with MD simulations, which allows us to
 76 systematically investigate the role of different variables. In
 77 particular, we study the effects of the lattice parameter,
 78 dielectric permittivity of the interparticle space, and super-
 79 crystalline structure on the ionic fluxes. We show the
 80 emergence of nonohmic behaviors for large interparticle
 81 separations and provide an explanation based on the
 82 redistribution of the ions in the nonequilibrium steady state.
 83 Finally, we propose an example of a noncentrosymmetric
 84 NPSL formed by Janus bipolar NPs and use our model to
 85 demonstrate that this material exhibits current-rectifying
 86 properties. This type of nonreciprocal transport in a bulk
 87 material is very rare in electronic-conducting materials³⁷ and
 88 suggests that noncentrosymmetric NPSLs can be used for the
 89 construction of ionic diodes.

90 ■ THEORETICAL METHODS

91 **Description of the System.** We model a NPSL made of
 92 spherical NPs ($r = 5$ nm) coated by an end-grafted polymer, its
 93 counterions (K^+) and co-ions (Cl^-), and solvent molecules,
 94 see Figure 1. Each polymer chain has a single negative charge
 95 located in the segment adjacent to the surface. The rest of the
 96 polymer is neutral, and acts as a spacer of variable length,
 97 N_{neutral} . The solvent content of the system is fixed to an average
 98 volume fraction of $\langle \phi_s \rangle \approx 0.3$. The system is electroneutral,
 99 therefore, in the absence of added salt, the number of
 100 counterions (K^+) in the unit cell equals that of charged
 101 segments.

102 **Distribution of Polymer Segments.** We generate the
 103 structure of the system with a MOLT for NPSLs, similar to
 104 that previously described.^{33,38,39} MOLT explicitly includes
 105 structural details of the chemical species within the system and
 106 considers their conformational degrees of freedom. This tool
 107 provides the distribution of the polymer in equilibrium, Figure
 108 1b. The distribution of the charged polymer segments
 109 predicted by MOLT is then used as an input for the

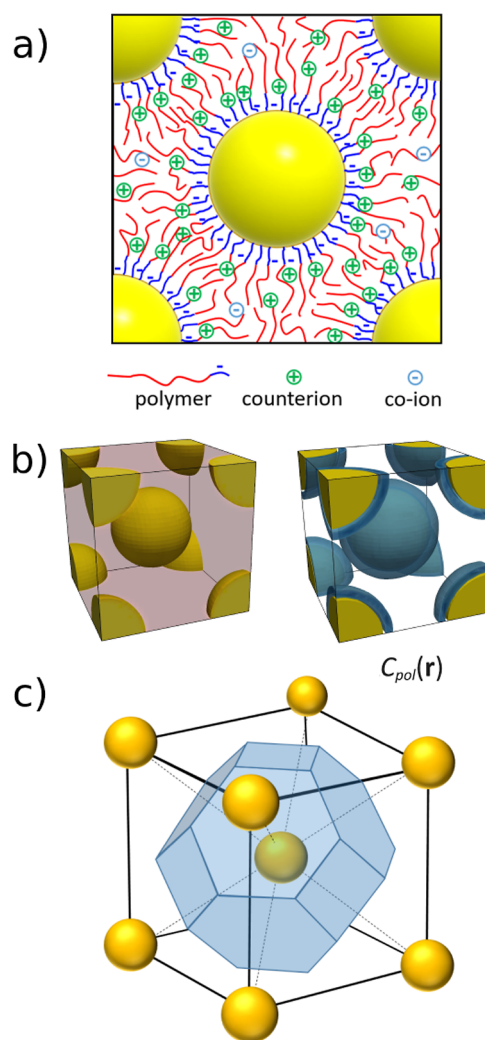


Figure 1. Schematic representation of the system under study. (a) Scheme of the (001) plane of a bcc NPSL modified by polymer chains. Neutral and negatively charged blocks are represented in red and blue, respectively. Positive counterions and negative co-ions are shown in green and blue, respectively. (b) Concentration of neutral spacers (red) and negatively charged segments (blue, C_{pol}) obtained from MOLT calculations. (c) Wigner–Seitz cell of the bcc NPSL, used as the unit cell of our simulations.

subsequent PNP calculations. It should be noted that MOLT
 calculations use cubic cells, which we trim to obtain the
 corresponding Wigner–Seitz cells (WS, see Figure 1c). The
 WS cells are then used to perform the PNP calculations (the
 technical advantages of this approach are discussed in the
 Supporting Information). Note also that because MOLT
 considers perfect packing of solvent, polymers, and NP cores,³⁹
 and we fix $\langle \phi_s \rangle$, the choice of the length of the neutral spacer
 unequivocally defines the volume of the WS cell (volume per
 NP), see Table 1. However, since different crystalline phases
 have different packing efficiencies, a given volume of the WS
 cell translates into different lattice constants for the cubic unit
 cells depending on the crystal phase. In order to compare
 different crystalline phases, we used WS cells of similar volume.

Model of Ion Transport in the System. Like previous
 MD simulations,^{31,32} we aim to calculate the bulk conductivity
 of the NPSL as a function of the electric field applied to the
 material. The fluxes of the mobile counterions in the system,

Table 1. Structure, Particles Per Cubic Unit Cell (NPs/Cell), Lattice Parameter of the Cubic Cell (a_L), Volume of the Wigner–Seitz Cell (V_{WS}), and Length of the Neutral Spacer Required to Obtain the Structure in MOLT Calculations ($N_{neutral}$) for all Systems Studied in this Work

structure	NPs/cell	a_L (nm)	V_{WS} (nm ³)	$N_{neutral}$
bcc	2	13.0	1099	8
bcc	2	18.0	2916	48
bcc	2	23.0	6084	119
fcc	4	16.38	1099	8
fcc	4	22.68	2920	48
fcc	4	28.98	6085	119
sc	1	10.32	1099	8
sc	1	14.29	2918	48
sc	1	18.26	6088	119

K^+ and Cl^- , are described at the level of the Nernst–Planck (NP) equation

$$J_i = -D_i \left[\nabla C_i(\mathbf{r}) + q_i C_i(\mathbf{r}) \frac{F}{RT} \nabla \psi(\mathbf{r}) \right] \quad (1)$$

where T is the temperature, F is Faraday's constant and R is the ideal gas constant. J_i , C_i , D_i , and q_i are the flux, concentration, diffusion coefficient, and charge of the ion i , respectively (where $i = K^+$, Cl^-). $\psi(\mathbf{r})$ is the electrostatic potential and $\mathbf{r} = (x, y, z)$ denotes a point in space. Since the space between particles has a large concentration of polymer chains and for the sake of simplicity, we neglect electroosmotic effects.

We consider only steady-state conditions in this work, so the following condition applies

$$\nabla \cdot J_i(\mathbf{r}) = 0 \quad (2)$$

We model transport through a bulk NPSL, therefore, the local concentrations of the ions and their fluxes within the unit cell must comply with the periodicity and symmetry of the lattice. The following periodic condition enforces the continuity of the ion fluxes at cell boundaries

$$J_i(\mathbf{r}_1) \cdot \hat{\mathbf{n}}_1 = -J_i(\mathbf{r}_2) \cdot \hat{\mathbf{n}}_2 \quad (3)$$

where the points 1 and 2 are equivalent in the periodic system and reside on two opposing faces of the WS cell (faces 1 and 2, respectively, see pairs of opposing faces for the bcc WS cell in Figure S1 in the Supporting Information). $\hat{\mathbf{n}}_k$ is the exterior normal to the face k .

Ionic concentrations also fulfill the periodic boundary conditions

$$C_i(\mathbf{r}_1) = C_i(\mathbf{r}_2) \quad (4)$$

Note that in order to properly define the problem, the use of the boundary conditions, eqs 3 and 4, requires to constrain the numbers of K^+ and Cl^- ions in the unit cell to the values calculated from the fixed charge of the polymer and added salt. The nanoparticle cores are impenetrable objects for the ions; thus, the normal fluxes on their surfaces are zero

$$J_i(\mathbf{r}_{NP}) \cdot \hat{\mathbf{n}}_{NP} = 0 \quad (5)$$

where $\mathbf{r}_{NP}$ is a position at the surface of the nanoparticle core.

The electrostatic interactions in the system are treated with the mean-field Poisson equation

$$\nabla^2 \psi(\mathbf{r}) = -\frac{C_V(\mathbf{r})}{\epsilon \epsilon_0} \quad (6)$$

where ϵ_0 and ϵ are the dielectric permittivity of vacuum and the relative dielectric permittivity, respectively. We assume ϵ to be position-independent. $C_V(\mathbf{r})$ is the charge concentration, given by

$$C_V(\mathbf{r}) = F[C_{K^+}(\mathbf{r}) - C_{Cl^-}(\mathbf{r}) - C_{pol}(\mathbf{r})] \quad (7)$$

where C_{pol} is the (molar) concentration of negative charges from the polymer (see scheme in Figure 1).

While the concentrations are periodic in the system, the electrostatic potential is not because there is an applied electric field in a given direction. In nonequilibrium MD simulations, this electric field generates an external force acting over charged particles,⁴⁰ namely, $\mathbf{F}_i = -\nabla U^{int}(\{\mathbf{r}\}) + q_i \mathbf{E}$, where q_i is the charge of particle i , $\mathbf{E}$ is the constant external field vector, and $U^{int}(\{\mathbf{r}\})$ is the force-field potential energy that depends only on the relative positions of all particles in the system, $\{\mathbf{r}\}$, and thus, it is a periodic function in the crystal. In analogy, we split here the total electric field, $-\nabla \psi$, into two components

$$-\nabla \psi(\mathbf{r}) = -\nabla \psi^{int}(\mathbf{r}) + \mathbf{E} \quad (8)$$

where ψ^{int} is the electrostatic potential generated by the ions and NP charges and depends only on the ion distribution in the unit cell. Therefore, ψ^{int} is a periodic function inside the crystal. Since $\mathbf{E}$ is constant, it is straightforward to show that if ψ (defined according eq 8) is a solution of the Poisson equation, then ψ^{int} is also a solution. Note also that ψ^{int} indirectly depends on $\mathbf{E}$ because ions reorganize in response to the external field, as we show in the Results and Discussion section. Equation 8 allows us to obtain the boundary condition on the surface of the WS cell. Integrating this equation between the points 1 and 2 that are equivalent due to the translational symmetry of crystal, results in

$$\psi(\mathbf{r}_1) - \psi(\mathbf{r}_2) = \psi^{int}(\mathbf{r}_1) - \psi^{int}(\mathbf{r}_2) + \mathbf{E} \cdot (\mathbf{r}_2 - \mathbf{r}_1) \quad (9)$$

Here, we used the fact that $\mathbf{E}$ is constant. Taking into account that the second term on the right-hand side vanishes because ψ^{int} is a periodic function, we reorganize eq 9 to obtain the PBC for ψ

$$\psi(\mathbf{r}_1) + \mathbf{E} \cdot \mathbf{r}_1 = \psi(\mathbf{r}_2) + \mathbf{E} \cdot \mathbf{r}_2 \quad (10)$$

This boundary condition requires to specify the arbitrary zero of the electrostatic potential. For example, for the WS bcc cell, the center point of the lower square base is set to $\psi = 0$.

A zero-charge boundary condition is imposed on the nanoparticle surface

$$\nabla \psi(\mathbf{r}_{NP}) \cdot \hat{\mathbf{n}}_{NP} = 0 \quad (11)$$

This condition also assumes that the dielectric constant of the NP is much smaller than that of the solution. The mean ionic flux in the system, $\bar{J}$, is obtained from the following expression

$$\bar{J} = \frac{F}{V_{cell}} \int [J_{K^+}(\mathbf{r}) - J_{Cl^-}(\mathbf{r})] dV \quad (12)$$

where the integral runs over the volume of the unit cell, V_{cell} (fluxes are zero within the NP core). The ionic flux obtained in this way is parallel to the direction of the applied electric field. In the Supporting Information, we show that its magnitude, $\bar{J}$, is equivalent to taking an average of $[J_{K^+}(\mathbf{r}) - J_{Cl^-}(\mathbf{r})] \cdot \hat{\mathbf{n}}$ over a

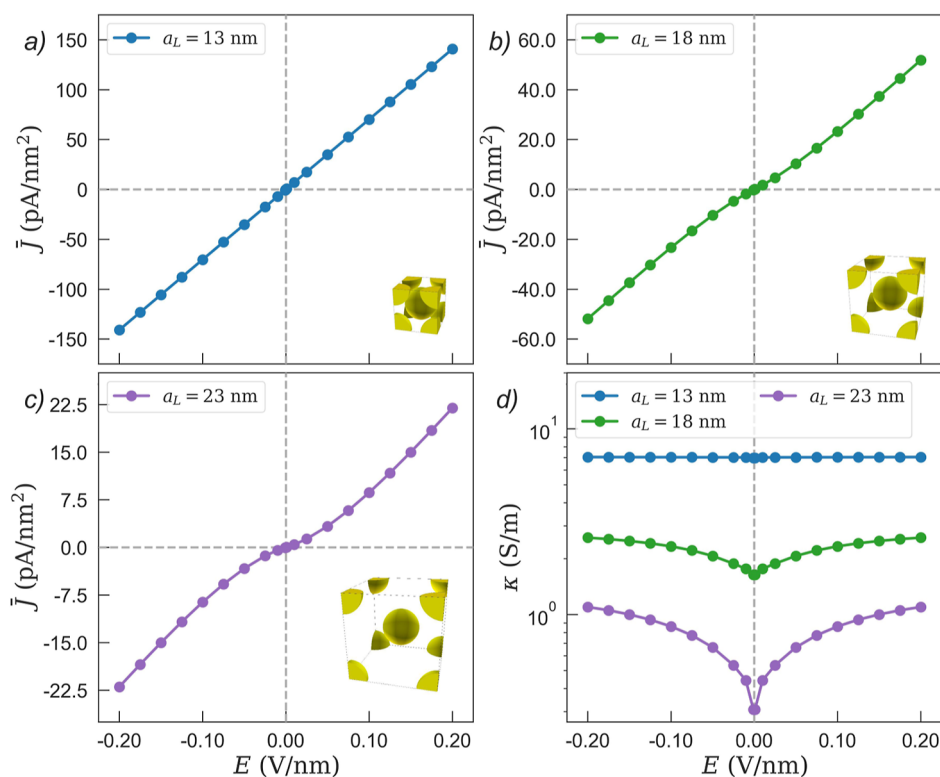


Figure 2. Ionic flux as function of an electric field applied in the direction [001] in a bcc superlattice with different cell parameters: (a) 13, (b) 18, and (c) 23 nm. (d) Conductivity vs electric field for the same systems in (a–c). Calculation parameters: nanoparticle radius: 5 nm; polymer surface coverage, $\sigma = 0.5$ nm⁻²; and dielectric constant of the interparticle media, $\epsilon = 10$.

plane perpendicular to the direction of the applied electric field. For a discussion about the technical convenience of using eq 12 instead of averaging the fluxes over such plane, see the Supporting Information.

Different methods have been used in the past to solve the PNP equations, such as finite differences,²⁶ finite elements,²⁷ the network approach,³⁰ and approximate analytical models.^{21,28} We solved the system of coupled nonlinear partial differential equations composed by eqs 1–12 using the finite element method (FEM) implemented in Comsol Multiphysics v5.2. The diffusion coefficients for both ions were fixed to 1.0×10^{-9} m²/s. Note, however, that D_i is a multiplicative factor in eq 1, and, therefore, modifying D_i (using the same value for K⁺ and Cl⁻) only introduces a multiplicative factor in the predicted ion fluxes. Further details about the FEM implementation are provided in the Supporting Information.

RESULTS AND DISCUSSION

Ionic Conductivity of NPSLs. We investigate superlattices of nanoparticles modified by polymer brushes. The segment of each polymer that is tethered to the nanoparticles bears a negative charge. The remaining segments are neutral and fulfill the role of a spacer, i.e., they are introduced in order to allow control over the interparticle distance by varying the number of neutral segments (see Figure 1a). This NP design is similar to that used for NP-single ion electrolytes, which also combine charged groups next to the surface with long neutral polymeric spacers.^{18,19} We fixed the average volume fraction of the solvent for all systems studied to $\langle \phi_s \rangle = 0.3$ (in our model, using other values will simply change the length of the polymeric spacers required to obtain a given lattice parameter).

Table 1 compiles the lengths of the neutral spacer and corresponding lattice sizes for all systems under study.

We start discussing systems without added salt, where the number of K⁺ ions is equal to the number of charged segments in order to ensure the electroneutrality. Figure 2a–c displays the magnitude of the ionic flux ($\bar{J}$) for this system as a function of the magnitude of the applied electric field (E) for different lattice parameters (which are obtained by varying the length of the neutral block according to Table 1). Figure 2d shows the corresponding conductivities ($\bar{J}/E$) versus E . The range of electric fields under study (−0.2 to 0.2 V/nm) is within that typically used in electronic/chemoelectronic applications,^{9–12,41,42} and results from applying a large potential bias to a thin film. This range is also similar to that used in previous MD studies of transport in NPSLs.^{31,32} On the other hand, it should be noted that these electric fields are around 6 orders of magnitude larger than those typically experienced by electrolytes in solid-state batteries;⁴³ thus, the nonohmic behaviors discussed here are not relevant for such applications.

Figure 2 shows that increasing the cell parameter has two significant consequences: first, a decrease in the ionic flux, and second, a nonohmic $\bar{J}$ – E response, i.e., the conductivity increases with applied electric field. In order to estimate the nonlinear contribution to the ionic flux we fitted the $\bar{J}$ – E curves with a polynomial function $\bar{J}(E) = \alpha E + \beta E^3$, where the quadratic term is omitted due to the symmetry of the curve with respect to the applied electric field (see the predictions of the analytical model below). The αE term represents the ohmic contribution to the flux, while βE^3 is the nonohmic contribution. In order to compare the different curves, we calculate the minimum electric field needed for the nonlinear term to represent a 10% of the total ionic flux, $E_{10\%}^{\text{NL}} = (\alpha/280$

281 $9\beta)^{1/2}$. The lower the value of $E_{10\%}^{\text{NL}}$, the larger is the deviation
 282 from the ohmic response because the nonlinear behavior
 283 appears at a lower applied field. Table 2 compiles $E_{10\%}^{\text{NL}}$ for the

Table 2. $E_{10\%}^{\text{NL}}$ for the Data in Figures 2 and 4

a_L (nm)	ϵ	$E_{10\%}^{\text{NL}}$ (V·nm ⁻¹)	α (pA·V ⁻¹ ·nm ⁻¹)	β (pA·V ⁻²)	$\alpha^* a_L^3$ (V·nm ²)
13	10	1.34	702.2	43.5	9128.2
18	10	0.16	222.1	998.3	3998.2
23	10	0.10	77.3	866.8	1778.3
23	20	0.14	77.3	866.8	2442.0
23	78.5	0.33	139.0	140.9	3195.9

284 different cell parameters. For $a_L = 13$ nm, $E_{10\%}^{\text{NL}} = 1.34$ V/nm,
 285 indicating that the nonohmic behavior is not significant within
 286 the range applied fields under study. However, for $a_L = 18$ and
 287 23 nm, $E_{10\%}^{\text{NL}}$ values are 0.16 and 0.10 V/nm, respectively.
 288 Therefore, in these cases, the nonohmic behavior is relevant in
 289 the range of electric fields under study.

290 The decrease in the ionic flux with increasing lattice
 291 parameter, a_L , is expected because the number of charge
 292 carriers (K^+) is constant and, therefore, their average
 293 concentration scales as $\sim a_L^{-3}$. Using this mean-concentration
 294 argument, the effective conductivity, $\bar{J}/E$ would scale as
 295 $\bar{J}/E \sim \alpha \sim a_L^{-3}$. However, Table 2 shows that αa_L^3 decreases
 296 with a_L and, therefore, the largest a_L have smaller
 297 conductivities than those expected from a simple mean-
 298 concentration argument. Moreover, the mean-concentration
 299 argument does not explain the nonohmic regimes for large E .
 300 Therefore, to better understand the transport mechanism in
 301 the NPSL, we should analyze the spatial distribution of the
 302 cations and its dependence on the applied field.

303 Figure 3 shows the cation concentration along the central
 304 axis of the WS cell (which is parallel to the applied field and
 305 shown in dotted lines in the right panels) for 0 V/nm
 306 (equilibrium conditions, blue solid line) and 0.2 V/nm (green
 307 line). The red dashed line shows the concentration of charged
 308 segments, C_{pol} , which is assumed to be independent of the
 309 applied field because the charged segments are directly
 310 tethered to the NP core and, thus, lack conformational
 311 freedom. The right panels show color maps of the cation
 312 concentration along a cut of the WS cell. For the smallest cell
 313 parameter (Figure 3a), there is an almost homogeneous and
 314 field-independent cation distribution over the WS cell. In this
 315 scenario, the cationic clouds surrounding the NPs in
 316 neighboring WS cells fully overlap, which results in high
 317 conductivity and a fully ohmic behavior (Figure 2).

318 As the interparticle distance increases, an insulating region
 319 with low concentration of cations develops between particles
 320 (see Figure 3b,c). The localization of the cations near the NP
 321 surfaces not only increases the resistance of the system but also
 322 it leads to the emergence of the nonlinear behavior: in the
 323 presence of an electric field, the K^+ density becomes
 324 asymmetrically distributed with respect to the nanoparticle
 325 core. This redistribution of the cation density increases the
 326 ionic concentration in the interparticle region along the
 327 direction of the applied field, and, therefore, reduces the
 328 resistance of the system. This concentration–polarization
 329 effect is proportional to the applied field, so the conductivity
 330 increases with E (Figure 2d), i.e., there is a positive deviation
 331 from Ohm's law. Interestingly, similar positive deviations from

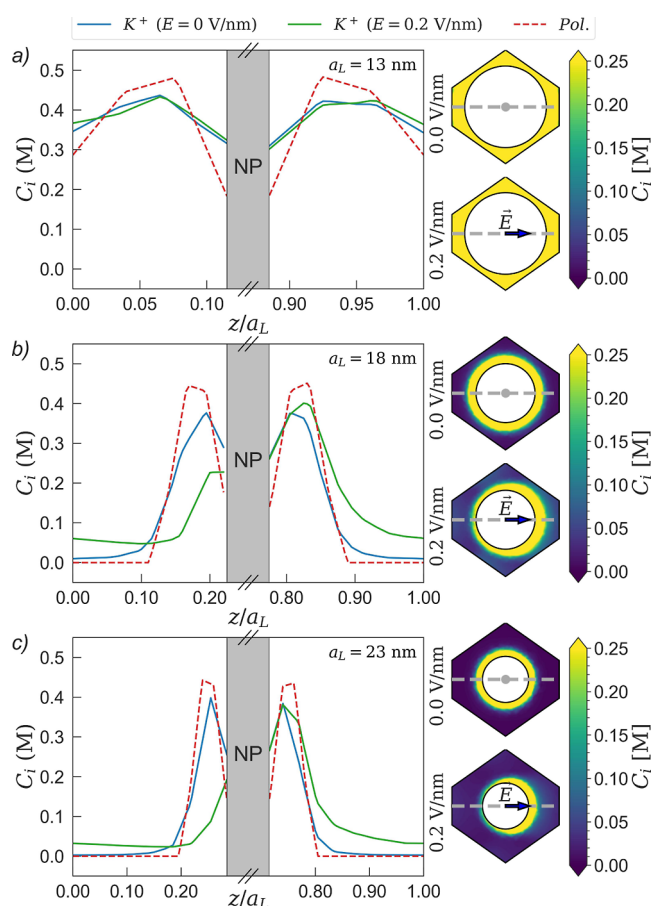


Figure 3. Concentration profiles as a function of the reduced distance z/a_L for the charged segment of the polymers (red dashed line) and the K^+ counterions for $E = 0$ and 0.2 V/nm (in blue and green, respectively). Calculations correspond to an electric field applied in the [001] direction and different cell parameters: (a) $a_L = 13$, (b) $a_L = 18$, and (c) $a_L = 23$ nm. The right panels show color maps of the K^+ concentration for a cut [(110) plane] of the WS cell. Other calculation parameters as in Figure 2.

Ohm's law have been observed for hourglass nanochannels,^{44,45} which show convex surfaces like NPs.

In Figure 4, we show the effect of the relative dielectric permittivity of the interparticle media, ϵ , on the ionic conductance of a bcc superlattice with $a_L = 23$ nm. Figure 4a shows the $\bar{J}$ – E curves for $\epsilon = 10$, 20, and 78.5. Increasing the dielectric permittivity produces an increase of the ionic current and of the linearity of the $\bar{J}$ – E response. Both effects can be understood from the electrostatic interactions between the charged segments and their counterions, as discussed next.

The top panel of Figure 4b shows that for $\epsilon = 10$ the counterions are strongly bounded to the polymer charges, causing $C_{K^+}(0 \text{ V/nm})$ to decay to almost zero near to the edge of the WS cell. As in the cases analyzed in Figure 3, this cation distribution results in a low ionic conductance. Increasing the applied electric field displaces the counterions at the edges of the unit cell [see curve for $C_{K^+}(0.2 \text{ V/nm})$] and produces a nonlinear behavior ($E_{10\%}^{\text{NL}} = 0.10 \text{ V/nm}$).

For $\epsilon = 78.4$, the electrostatic interactions between the polymer charges and their counterions are significantly reduced, which lowers the energetic barrier for separating oppositely charged species. Figure 4b shows that in these conditions, there is a significant concentration of counterions

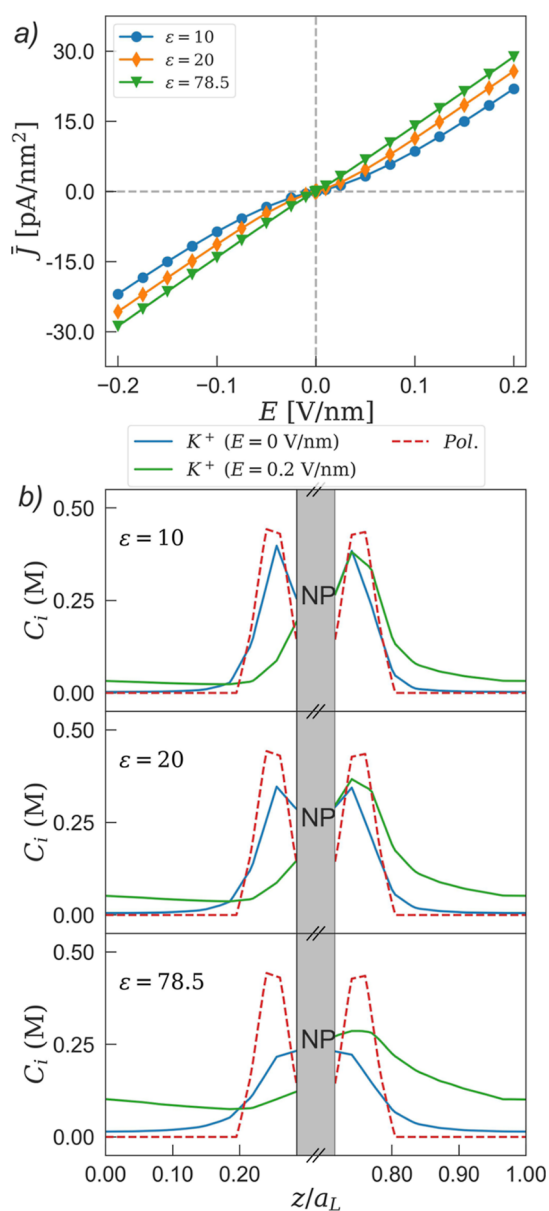


Figure 4. (a) Effect of the dielectric permittivity of the interparticle media, ϵ , on the $\bar{J}$ – E for a bcc superlattice. (b) Concentration of positive counterions for $E = 0$ and 0.2 V/m (blue and red lines, respectively) as a function of the reduced distance z/a_L in the direction [001] of the bcc superlattice. The red dashed lines show the concentration of the charged segments. Calculation parameters: $a_L = 23$ nm, other parameters as in Figure 2.

at the edges of the WS cell (i.e., the ionic clouds surrounding neighbor NPs overlap). Moreover, the effect of the electric field on the counterion distribution is reduced with respect to the case of $\epsilon = 10$, which results in an ohmic behavior in the whole range of electric fields under study ($E_{10\%}^{\text{NR}} = 0.33$ V/nm). The increase in the counterion concentration in the interparticle region boosts the maximum ionic current that the system can sustain, reaching a value of ≈ 30 pA/nm² at 0.2 V/nm.

A systematic study of the role of the supercrystalline structure and direction of the applied field is presented in the Supporting Information and briefly discussed here. We calculated the $\bar{J}$ – E curves for an electric field applied to the [001] direction of bcc, fcc, and sc structures. Comparing

systems with the same volume per WS cell results in rather small differences among the three crystal phases (<15%, see Figure S6 in the Supporting Information). This result is explained as follows. For small interparticle distances, the counterion clouds overlap and, therefore, the transport is controlled by the average cation concentration (which only depends on the volume of the WS cell). On the other hand, for large WS volumes, the separation between particles is large and, therefore, the local crystalline order does not play an important role. We also observed almost no differences in the $\bar{J}$ – E curves when applying the electric field along different directions ([001], [110], and [111]) of the bcc lattice (Figure S5 in the Supporting Information).

So far, we analyzed NPSLs in the absence of added salt. Figure 5a shows the $\bar{J}$ – E curves for 0, 50, and 100 mM of

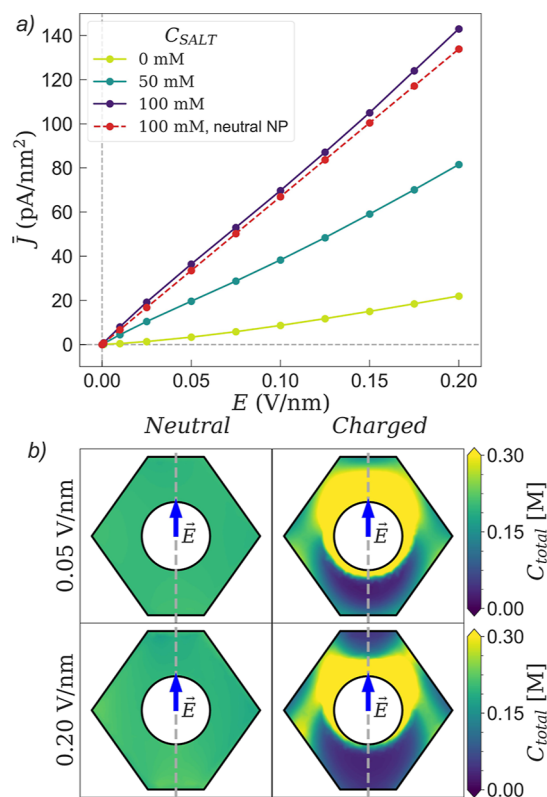


Figure 5. (a) Effect of added salt on the $\bar{J}$ – E curves for the bcc superlattice with $a_L = 23$ nm. The red dashed line shows the behavior of a NPSL formed by neutral NPs. (b) Color maps of the total ionic concentration (K^+ and Cl^-) along the (110) plane of the bcc WS cell for charged and neutral NPs and different values of E . Other calculation parameters as in Figure 2.

added KCl. As expected, adding salt increases the conductivity due to the increase in the number of mobile ions. We also plot in this figure a $\bar{J}$ – E curve for a system with neutral NPs (no charged polymer segments) and 100 mM of added KCl, which results in a total ion concentration of 200 mM (100 mM of K^+ and 100 mM of Cl^-). Interestingly, for 100 mM of added KCl, the lattices made of neutral and charged NPs exhibit almost the same conductivity, which is unexpected because the latter has almost 1.5 times the number of K^+ ions due to the additional K^+ counterions added to neutralize the NP charges (additional results are presented in Figure S7 in the Supporting Information). To understand this behavior, we plot in Figure 5b the ion distribution for different values of E and surface

charges. For the charged NPs and $E = 0.2$ V/nm, an ion depletion zone forms in the interparticle region, which explains the smaller-than-expected ionic flux in this case. This behavior is similar to the concentration–polarization effect observed in nanopores, which leads to the formation of depletion and accumulations zones of mobile ions at the entrance and the exit of the nanopore, respectively.^{35,46,47} This concentration–polarization effect reduces the conductance of the pore.

Analytical Results from a Perturbation Analysis. The complexity of ion transport in NPSL precludes the development of exact analytical models; therefore, we resorted above to numerical calculations to understand the underlying mechanisms. However, in this section, we present some general analytical results obtained with an approximate model. We consider the case of a NPSL in the presence of counterions (i.e., no added salt) and make a 1D approximation, where all functions are assumed to depend only on the z coordinate (which is aligned to the direction of the applied field). For example, under this assumption, the concentration of fixed polymer charges becomes $C_{\text{pol}}(z)$. This function can be in principle obtained by averaging $C_{\text{pol}}(\mathbf{r})$ in the x, y plane. Given the symmetry of the lattice, $C_{\text{pol}}(z)$ and $C_{\text{K}^+}(z)$ are periodic functions [$C_i(z + L) = C_i(z)$], where L is the size of the unit cell. We will further assume that $C_{\text{pol}}(z)$ is symmetric with respect to the center of inversion of the lattice [$C_{\text{pol}}(L - z) = C_{\text{pol}}(z)$], as is the case for the NPSLs studied so far (centrosymmetric lattices). Even with these approximations, the analytical problem cannot be exactly solved, but admits a series of expansions using a perturbation parameter. We discuss here the main results of this approach and provide an extensive derivation in the [Supporting Information](#).

We choose $\gamma = L\epsilon_0 RT N_A F^{-2}$ as the perturbation parameter, where N_A is Avogadro's number. Analyzing a series expansion of E versus $\bar{J}$ up to $O(\gamma^2)$ yields the following equation

$$E = \frac{L^3 RT N_A}{DF} [\bar{J} (R_{0,1} + \gamma R_{1,1} + \gamma^2 R_{2,1}) + \bar{J}^3 (\gamma^2 R_{2,3})] \quad (13)$$

where R_{ij} are constants that depend only on integrals of the distribution of fixed charges in the system, C_{pol} , over the unit cell. There are a few general conclusions that can be drawn from eq 13.

1. Equation 13 has no quadratic term in $\bar{J}$, which is a direct consequence of assuming a symmetric C_{pol} in the unit cell and it is consistent with the results shown in the previous section. In the next section, we show that an asymmetric C_{pol} can result in ion-current rectifying NPSLs.

2. Keeping only terms up to $O(\gamma)$ and rearranging results in

$$J = \frac{DF}{RT N_A L^3} \frac{E}{(R_{0,1} + \gamma R_{1,1})} \quad (14)$$

with $R_{0,1} > 0$ and $R_{1,1} < 0$ (see proof in the [Supporting Information](#)). Therefore, increasing the dielectric constant (i.e., increasing γ) at fixed E results in an increase in $\bar{J}$, in agreement with the results in [Figure 4](#).

3. The nonlinear $\bar{J}^3$ term depends on $R_{2,1}$, which is strictly negative (see the [Supporting Information](#)). Therefore, the deviations from linearity in the $\bar{J}$ – E curves for

NPSLs are strictly positive (the conductance increases with E).

Assuming that the 1D approximation correctly captures the behavior of the 3D NPSLs, these three conclusions are of general validity for any centro-symmetric superlattice.

Current-Rectification in NPSL of Janus Particles. Let us now consider a noncentro-symmetric superlattice that has an asymmetric charge distribution in the unit cell: a bcc lattice of Janus NPs, see inset in [Figure 6a](#). In these asymmetric NPs,

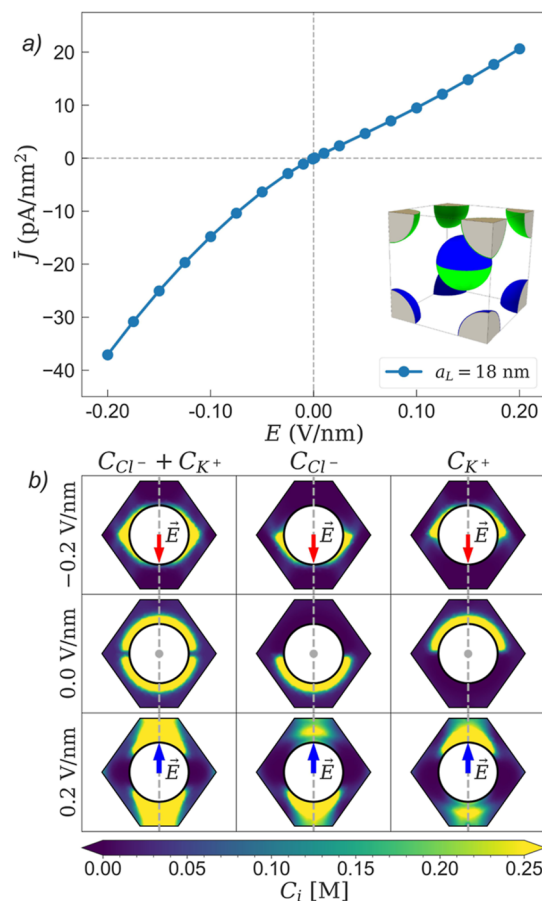


Figure 6. (a) $\bar{J}$ – E curve for a bcc NPSL with $a_L = 18$ nm formed by Janus bipolar nanoparticles. The inset shows the charge distribution in the cubic bcc lattice, blue and green regions are negatively and positively charged, respectively. (b) Color maps of the concentration of K^+ , Cl^- and their sum in the (110) plane of the unit cell for different applied electric fields. Other calculation parameters as in [Figure 2](#).

the charged segments attached to the surface are negative (-1 charge per segment) in the upper hemisphere and positive ($+1$ charge per segment) in the lower one. K^+ and Cl^- ions are introduced into the calculation cell in an amount equal to the number of negative and positive fixed charges of the polymer, respectively. The applied electric field is aligned with the z axis. [Figure 6](#) shows that the $\bar{J}$ – E curve for this NPSL is asymmetric with respect to the direction of the applied electric field, i.e., the NPSL rectifies the ionic current. While current rectification in thin NP films has been reported before,²⁰ the results in [Figure 6](#) indicate the rectification of a bulk ionic current. This behavior is significantly more difficult to obtain due to the periodicity of the crystal.³⁷

Figure 6b shows color maps of the K^+ and Cl^- concentrations and their sum in the (110) plane of the WS cell, for different applied electric fields. In equilibrium, $\Delta V = 0$, the counterions are located near the charged surface of opposite sign to them. In the low-conductivity ("closed") branch of the $\bar{J}-E$ plot ($\Delta V = 0.2$ V/nm, bottom row in Figure 6) the electric field pulls the ions away from the particle. This results in a depletion region near the equator of the NP, which breaks the continuity of the ionic cloud in the direction of the applied field. This high-resistance region lowers the ionic conductivity. On the other hand, in the high-conductivity ("open") branch of the $\bar{J}-E$ curve ($\Delta V = -0.2$ V/nm, top row in Figure 6) the counterions move in the opposite direction that in the closed branch. This results in an accumulation of ions in the equatorial plane, which reduces the resistance of that region. While there is also a depletion zone in the interparticle space along the [001] direction (direction of the applied field), this depletion zone has a limited negative effect on conductivity since transport is still possible across the hexagonal faces of the WS cell.

Current rectification in the case of Figure 6 is analogous to that observed in charged bipolar nanopores, whose surface charge is positive in one-half of the pore and negative in the other.^{26,27} Like the case of the NPSLs, the open branch occurs in a bipolar pore when the cations enter the pore from the negative side of the membrane, which leads to the formation of an accumulation region at the middle of the pore.²⁶ The closed branch occurs when the ions move in the opposite direction and generate a depletion region within the pore.

The rectification factors, $\alpha_R = -\bar{J}(-0.2 \text{ V/nm})/\bar{J}(0.2 \text{ V/nm})$, for the NPSLs are 1.67, 1.80, and 1.15 for $a_L = 13, 18$, and 23 nm, respectively. This nonmonotonic trend contrasts with the monotonic decrease of α_R with pore length observed in nanopore bipolar diodes.²⁷

CONCLUSIONS

This work reports the first study of the bulk ionic conductivity of NPSLs using the 3D PNP equations. The computational efficiency of this approach allowed us to systematically study current-electric field curves for a large parameter space, including different lengths of polymer spacers (which translate into different lattice parameters), dielectric constants of the interparticle media, supercrystalline structure (bcc, fcc, and sc), direction of the applied field, presence of added salt, and noncentrosymmetric lattices based on Janus NPs. While the efficiency of the PNP method allows addressing problems too costly for MD simulations, it is important to mention the approximations involved, particularly the fact that it neglects ion-ion correlations. The PNP model and its equilibrium case, the Poisson-Boltzmann model, are known to properly capture the general physical behavior of charged surfaces interacting with monovalent ions.⁴⁸⁻⁵¹ In a particularly relevant work, Boda and co-workers compared the PNP approach with Monte Carlo simulations (which include ion correlations) for narrow (radius = 1 nm) bipolar nanopores and found excellent agreement between the ionic currents calculated between both techniques.⁵⁰ The case of multivalent ions was also studied,⁵² and it was shown that the PNP model fails to capture charge-inversion effects and to reproduce the effect of surface charge in current rectification. In summary, these previous works suggest that the neglecting ion-ion correlations is a valid approximation for monovalent electrolytes, but the PNP approach should not be applied to multivalent ions.

Based on their nonohmic ionic conductivity, NPSLs containing multivalent charge carriers have been proposed as an active material for ionic diodes.³¹ We show here that nonohmic behaviors can be obtained even for monovalent ions by using polymeric spacers. However, the field-induced conductivity changes reported in previous MD studies for multiple charged counterions^{31,32} are larger than those observed in this study for monovalent ions for NPs separated by polymer spacers, which may be ascribed to the differences in the transport mechanisms in the two systems. In previous MD simulations,^{31,32} the insulator-conductor transition occurred when the electric field was large enough to allow charge carriers to escape from the attraction well created by the lattice. This mechanism does not necessarily require a change in the local concentration of the charge carriers. On the other hand, in our system, the counterions have a single charge and, thus, they bind weakly to the negative charges of the NP. The introduction of polymeric spacers allows us to strongly localize the K^+ ions near the NP surface at low applied electric fields. At high electric fields, the concentration of K^+ in the interparticle space increases, leading to an increase in the conductivity of our system. Therefore, the nonohmic responses in our system necessarily require a redistribution of the ions in the nonequilibrium steady-state. We stress that the strong charge correlations between multivalent ions and surface charges that produce nonohmic behaviors in the system studied with MD by Lionello et al.³¹ cannot be captured by the PNP model. While ion-ion correlations may increase the nonlinearity of the $\bar{J}-E$ curves for monovalent ions as well, as we discussed in the previous paragraph such effect is expected to be much weaker than for the triple-charged ions considered in the MD study.^{48,52}

Bulk current rectification in electronic materials (known as polar conductors) requires noncentrosymmetric systems and it is a rather uncommon property.³⁷ In this work, we introduced the intriguing possibility of designing noncentrosymmetric NPSLs (based on Janus NPs) with current-rectifying ionic bulk conductivity. Such materials can find applications in chemoelectronic devices and diode-like elements in iontronic circuits.⁵³ Note that current rectification in semiconductor junctions (for electronic currents) or thin nanoporous membranes (for ionic currents) relies on the presence of interfaces to introduce an asymmetry in the system. In comparison, bulk current rectification in a crystal is a more intriguing concept because those interfaces are absent due to the periodicity of the material and, therefore, nonreciprocal currents can only arise in noncentrosymmetric systems.

The experimental realization of the superlattice of Janus NPs proposed here is certainly challenging, although it may be feasible in the future considering that the synthesis of small Janus NPs,⁵⁴ as well as their assembly in a NPSL^{55,56} have already been reported. Alternately, one can consider NPSLs of non-Janus NPs arranged in a noncentrosymmetric crystalline phase, such as wurtzite-like NPSLs.⁵⁷ We plan to theoretically analyze this possibility in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c02661>.

Numerical implementation of the finite element calculations, calculation of the mean ionic fluxes, 596

currents in equivalent directions due to symmetry, physical consistency and numerical precision checks, comparison between different (nonequivalent) directions of E in the bcc structures, comparison between different structures (bcc, fcc, and sc), and effect of salt concentration and analytical perturbative theory (PDF)

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Notes

The authors declare no competing financial interest.

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