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# Electronic Supplementary Information

## Formation of compounds with diverse polyelectrolyte morphologies and nonlinear ion conductance in a two-dimensional nanofluidic channel

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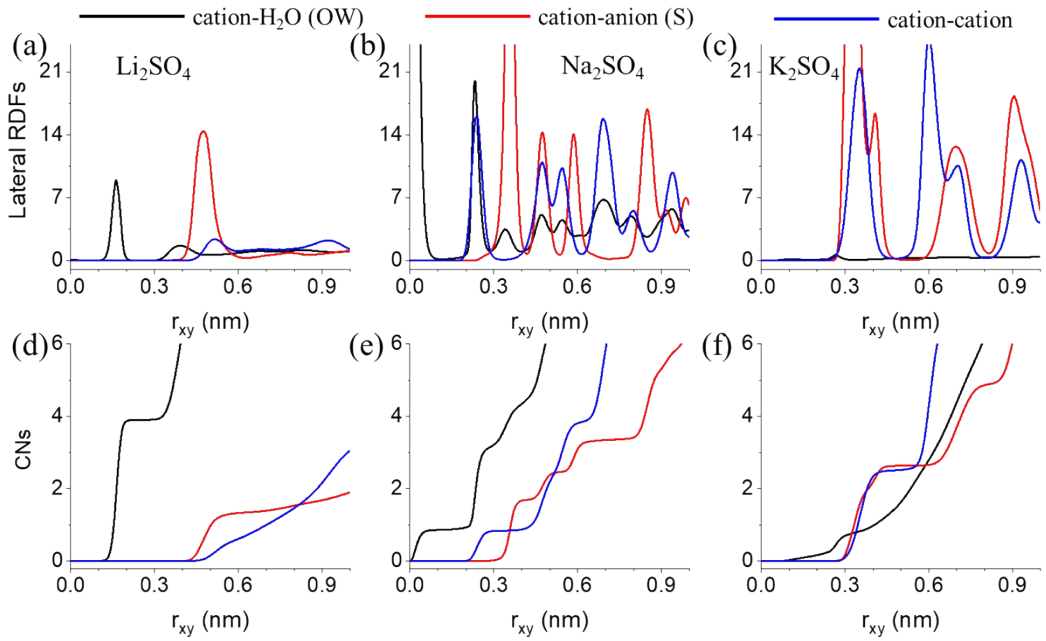


**Fig. S1.** (a-c) Lateral RDFs of cation-$H_2O$, cation-cation and cation-anion in the case of (a) $Li_2SO_4$ polyelectrolyte-like chains, (b) $4Na{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt, and (c) $K_2SO_4$ ionic crystal, respectively. (d-f) Corresponding CNs of the three polyelectrolytes.

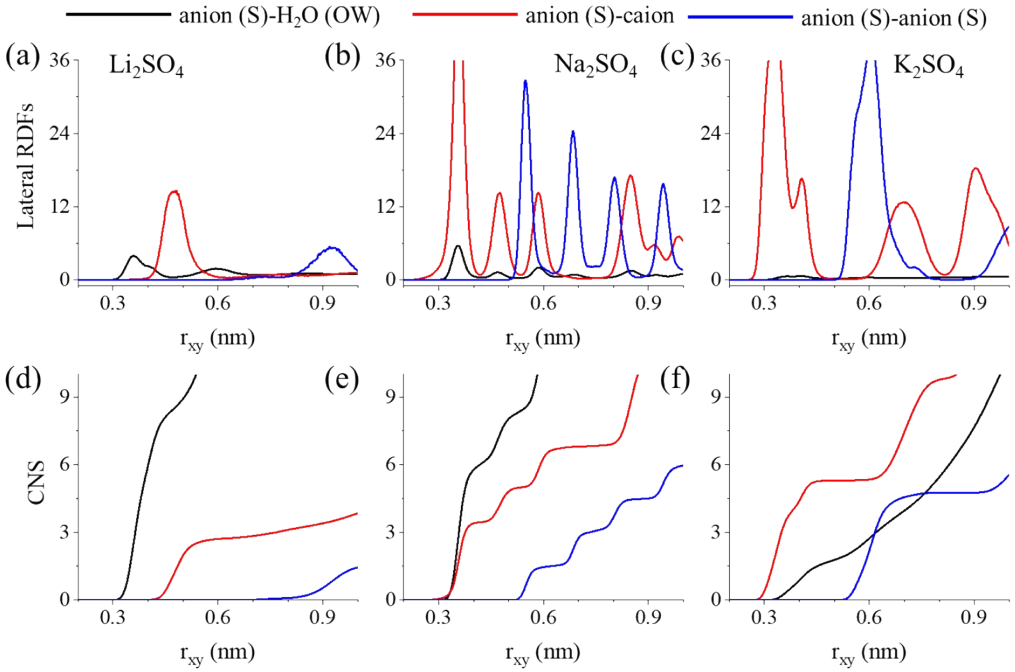


**Fig. S2.** (a-c) Lateral RDFs of anion-$H_2O$, anion-cation and anion-anion in the case of (a) $Li_2SO_4$ polyelectrolyte-like chains, (b) $4Na{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt, and (c) $K_2SO_4$ ionic crystal, respectively. (d-f) Corresponding CNs of the three polyelectrolytes.

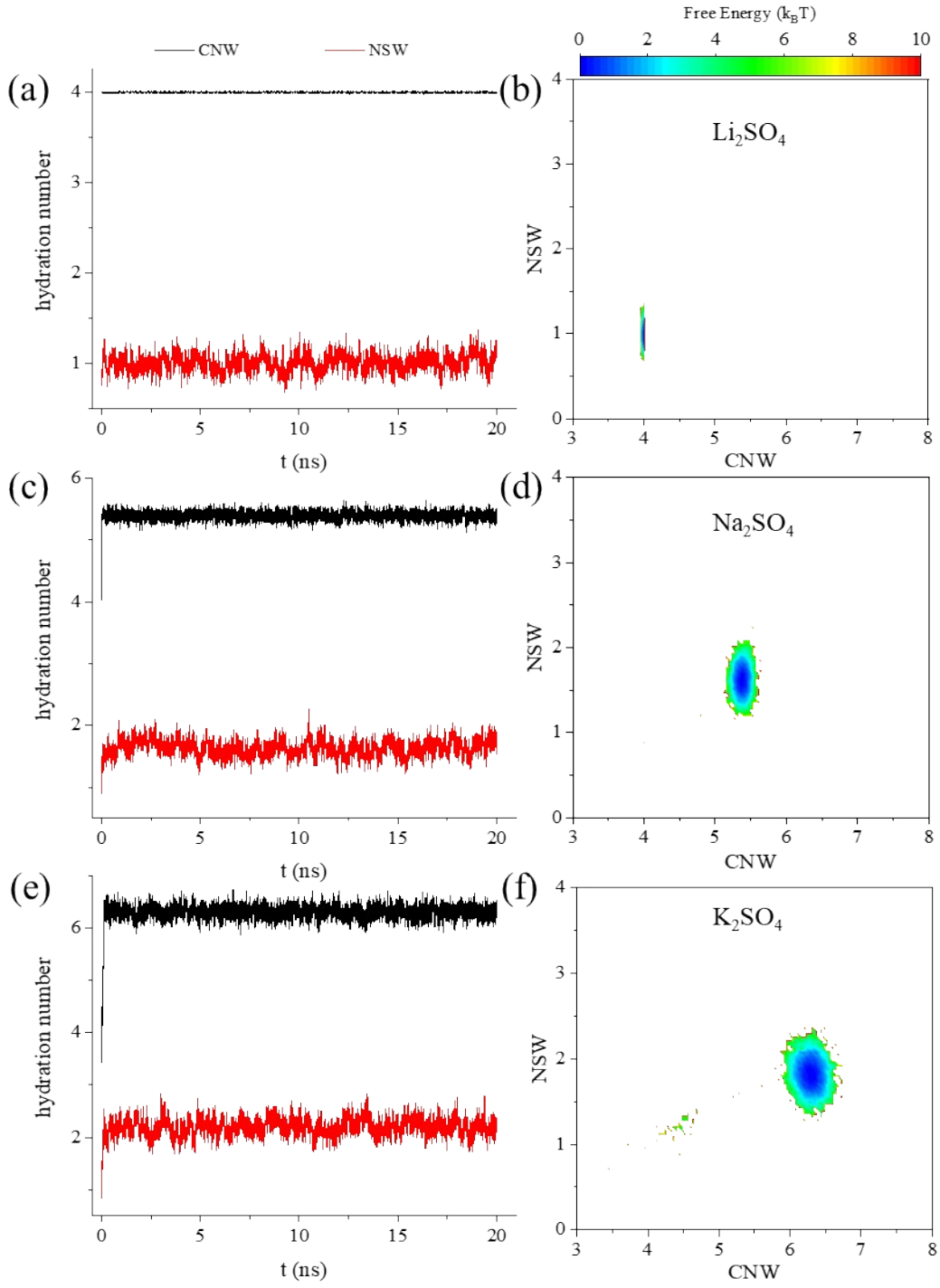


**Fig. S3.** The hydration number in bulk electrolyte solutions. The time-dependent average coordination number of water molecules (CNW) per cation and the number of shared water molecules (NSW) between cations and anions, computed based on representative snapshots during the 20 ns simulations of (a) $Li_2SO4$, (c) $Na_2SO4$ and (e) $K_2SO4$ aqueous solution in bulk. (b, d, f) The corresponding 2D conformational free energy landscapes.

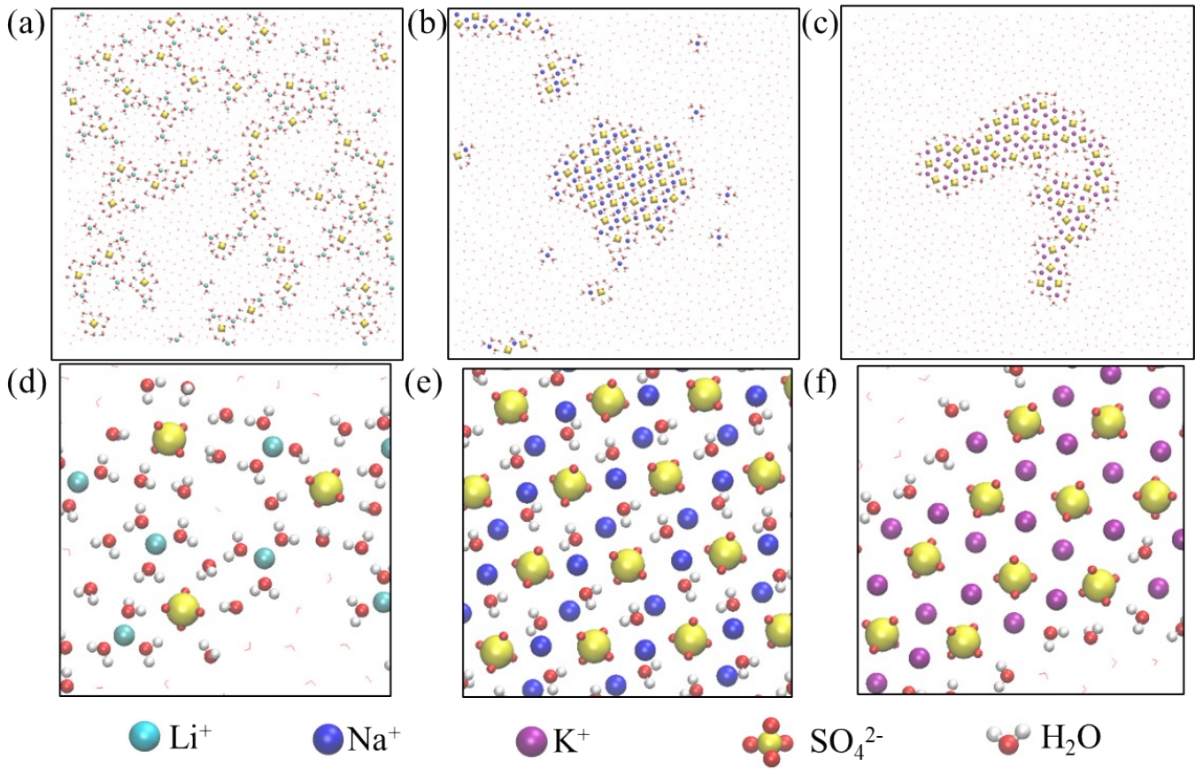


**Fig. S4.** Monolayer polyelectrolytes of alkali sulfates in the nanoslit with the width $D$ = 0.75 nm. Top views of snapshots of (a) $Li_2SO_4$ polyelectrolyte-like chains, (b) a $4Na{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt, and (c) a $K_2SO_4$ ionic crystal. (d-f) The corresponding magnified top view of a portion of the snapshots.

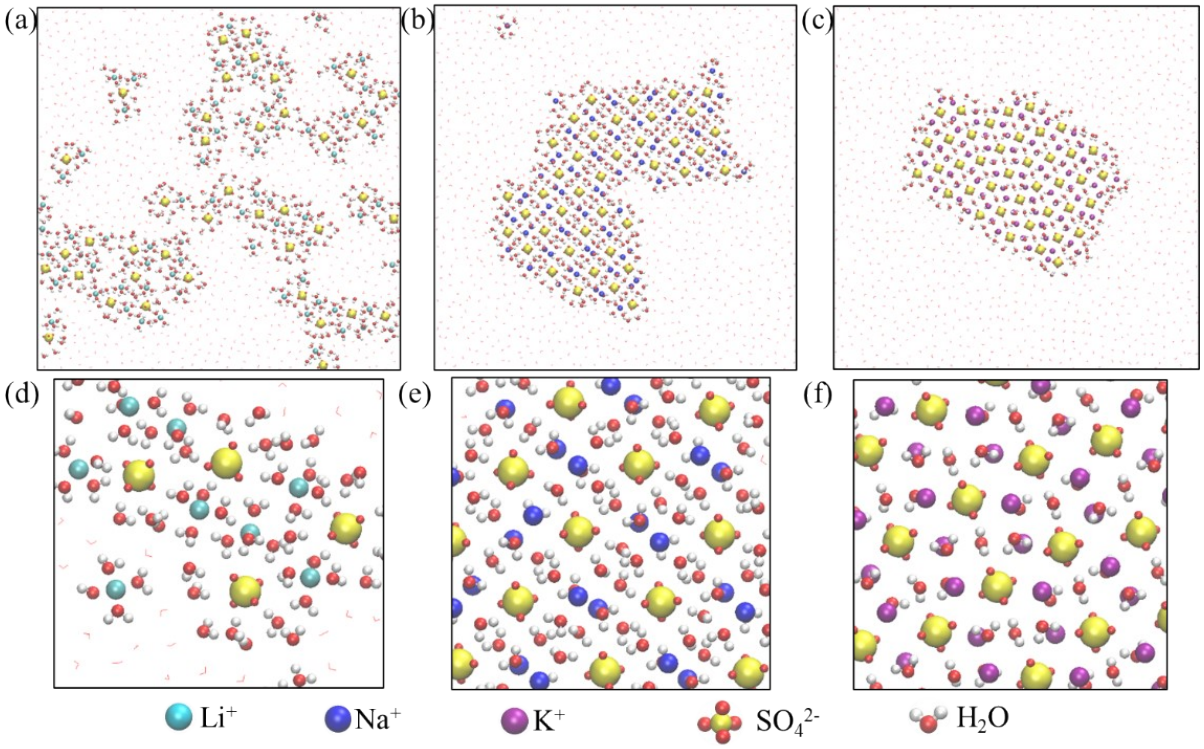


**Fig. S5.** Monolayer polyelectrolytes of alkali sulfates in the nanoslit with the width $D$ = 0.85 nm. Top views of snapshots of (a) $Li_2SO_4$ polyelectrolyte-like chains, (b) a $Na_2SO_4$·hydrated salt, and (c) a $4K{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt. (d-f) The corresponding magnified top view of a portion of the snapshots.

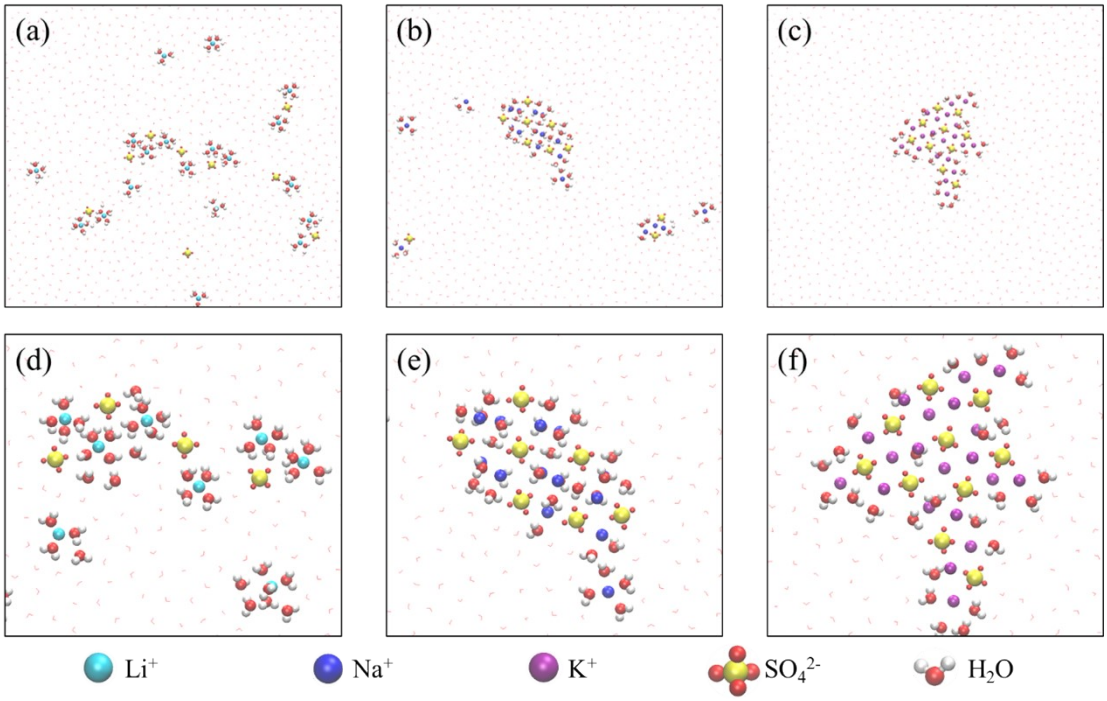


**Fig. S6.** Monolayer polyelectrolytes of alkali sulfates in the nanoslit with the width $D = 0.8$ nm with only 10 anions and 20 monovalent cations. Top views of snapshots of (a) $Li_2SO_4$ polyelectrolyte-like chains, (b) a $4Na{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt, and (c) a $K_2SO_4$ ionic crystal. (d-f) The corresponding magnified top view of a portion of the snapshots.

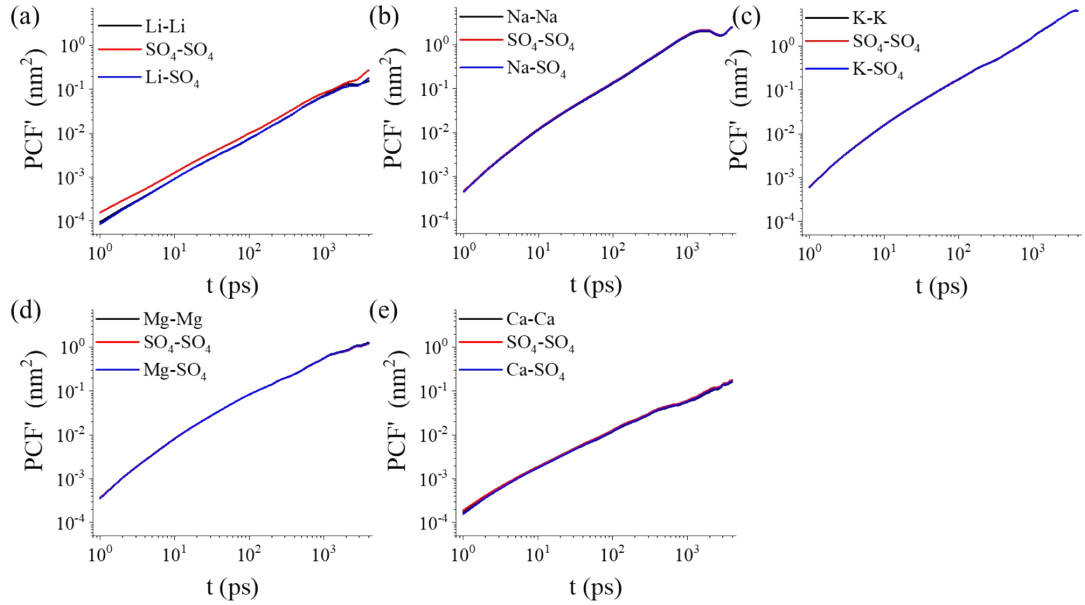


**Fig. S7.** The PCF' vs time for the (a) $Li_2SO_4$, (b) $Na_2SO_4$, (c) $K_2SO_4$, (d) $MgSO_4$, and (e) $CaSO_4$ aqueous solutions confined in the nanoslit. Here $PCF'_{ab}(t) = \langle [\vec{R}_a(t) - \vec{R}_a(0)] \cdot [\vec{R}_b(t) - \vec{R}_b(0)] \rangle$, and $PCF_{ab}(t) = \frac{V}{4k_BT} PCF'_{ab}(t)$ for the two-dimensional ionic aqueous solution.

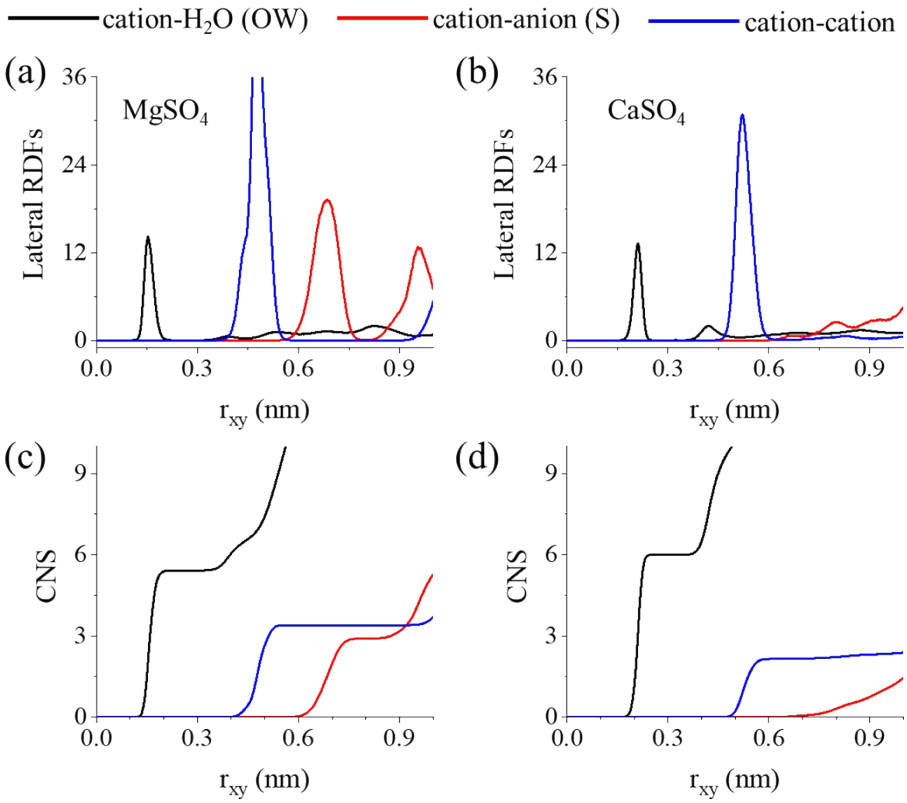


**Fig. S8.** (a-b) Lateral RDFs of cation-$H_2O$, cation-anion and cation-cation in the case of (a) $MgSO_4 \cdot 6H_2O$/$MgSO_4 \cdot 4H_2O$ hydrated salt and (b) $CaSO_4$ polyelectrolyte-like chains, respectively. c-d) Corresponding CNs of the two polyelectrolytes.

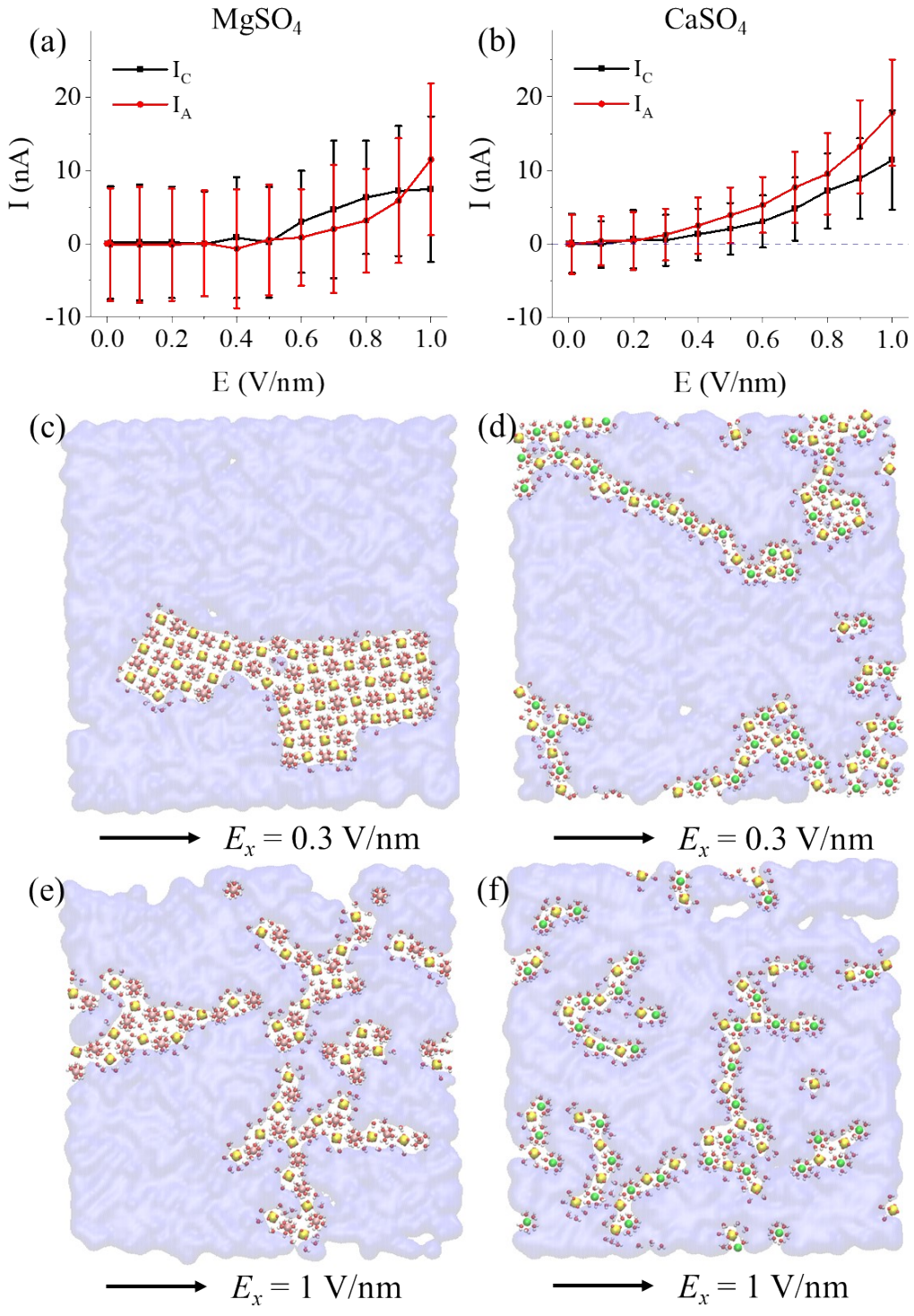


**Fig. S9.** Decomposition of ion current of (a) $MgSO_4$, and (b) $CaSO_4$ polyelectrolytes to cationic current ($I_C$) and anionic current ($I_A$), respectively. Corresponding snapshots under $E_x$ = 0.3 V/nm (c-d) and $E_x$ = 1 V/nm (e-f), respectively.

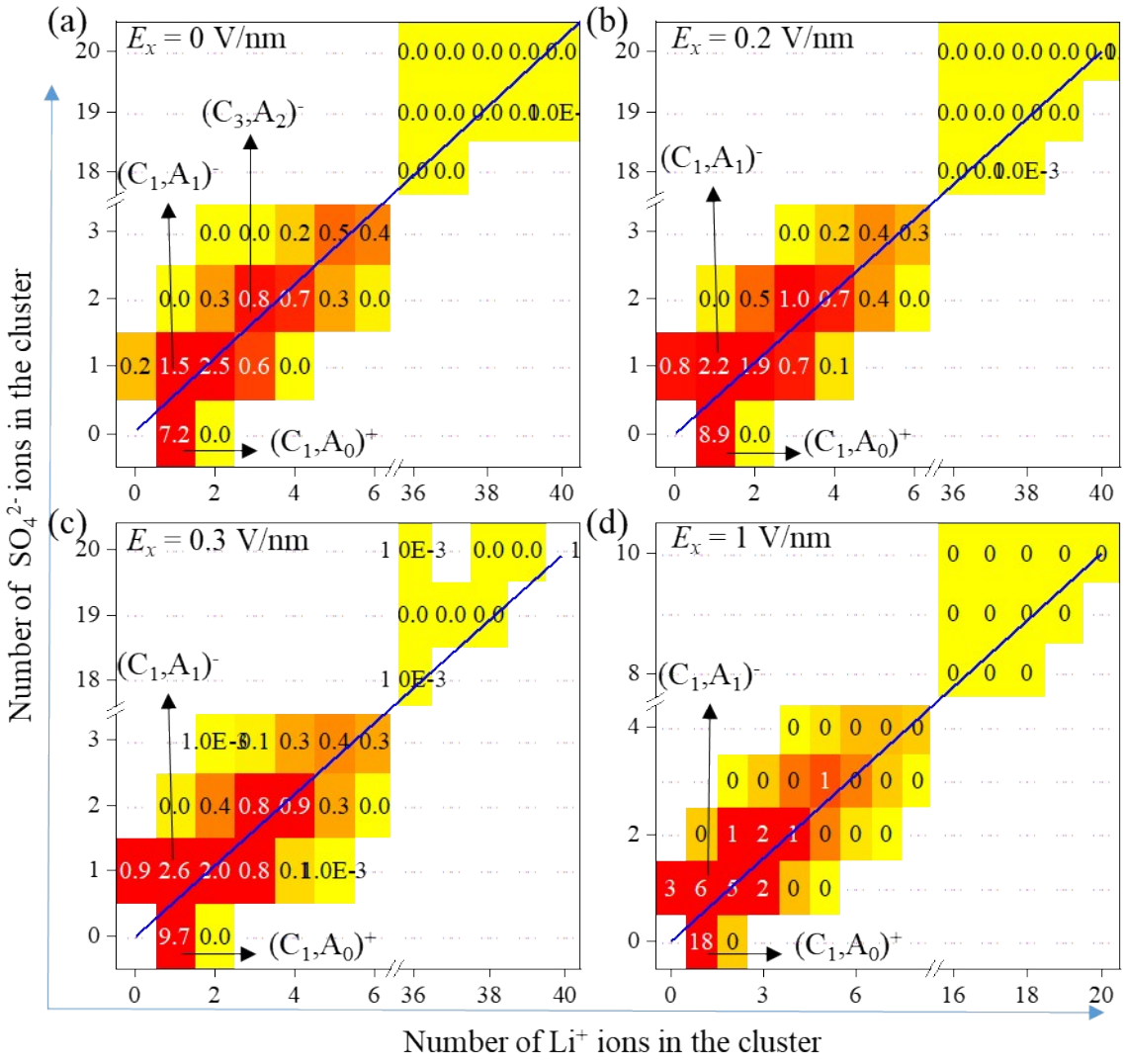


**Fig. S10.** Cluster distribution of the $Li_2SO_4$ system as a function of electric field $E_x$ = (a) 0 V/nm, (b) 0.2 V/nm, (c) 0.3 V/nm, and (d) 1.0 V/nm, respectively. The symbol $(C_i, A_j)^{i-2j}$ represented a cluster comprising $i$ Cations and $j$ Anions with a charge of $i$-2$j$. The number in the figures indicated the average number of a given cluster per snapshot. The blue oblique line $i = 2j$ suggested the neutral clusters.

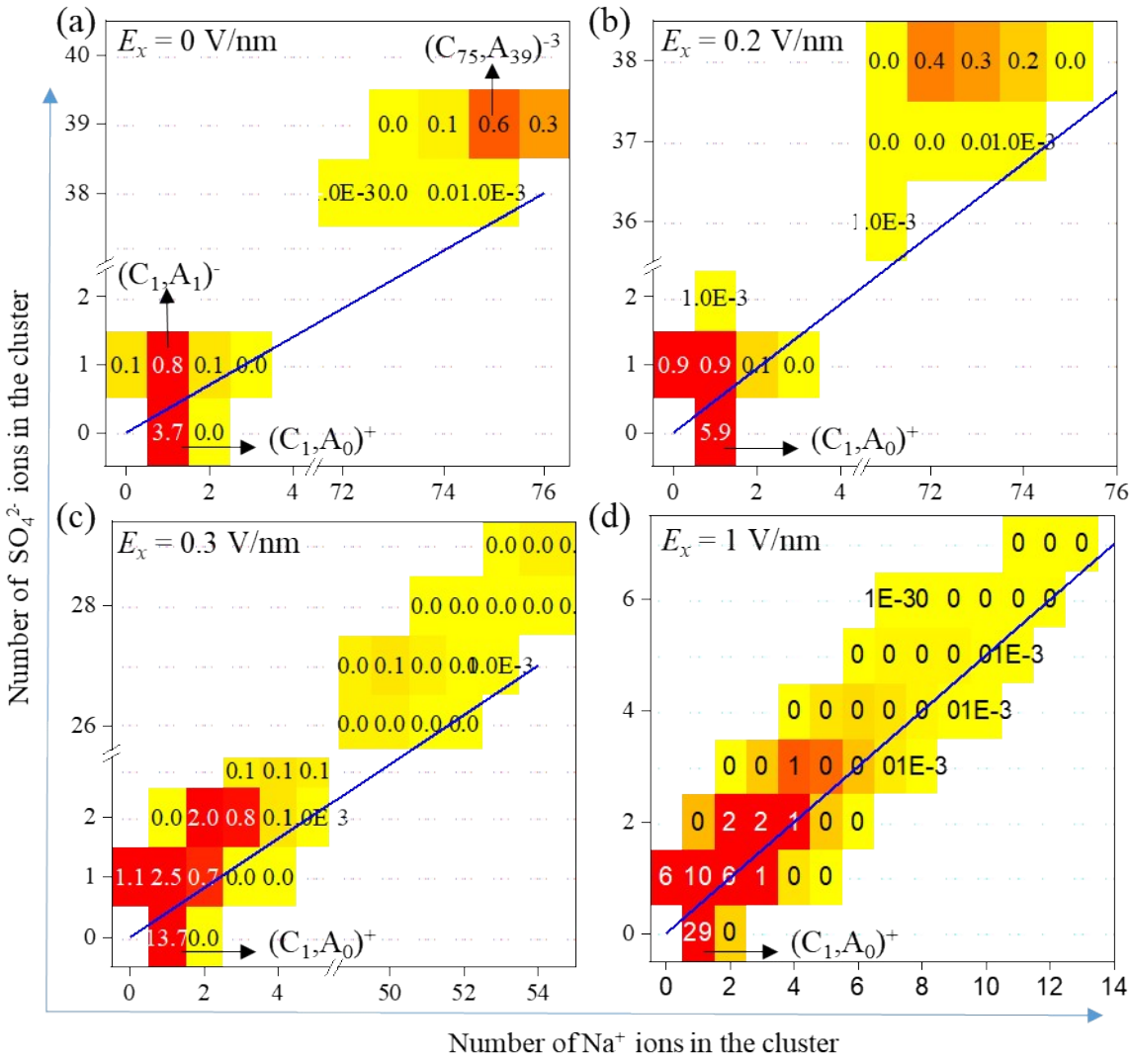


**Fig. S11.** Cluster distribution of the $Na_2SO_4$ system as a function of electric field $E_x$ = (a) 0 V/nm, (b) 0.2 V/nm, (c) 0.3 V/nm, and (d) 1.0 V/nm, respectively. The symbol $(C_i, A_j)^{i-2j}$ represented a cluster comprising *i* Cations and *j* Anions with a charge of *i*-2*j*. The number in the figures indicated the average number of a given cluster per snapshot. The blue oblique line $i = 2j$ suggested the neutral clusters.

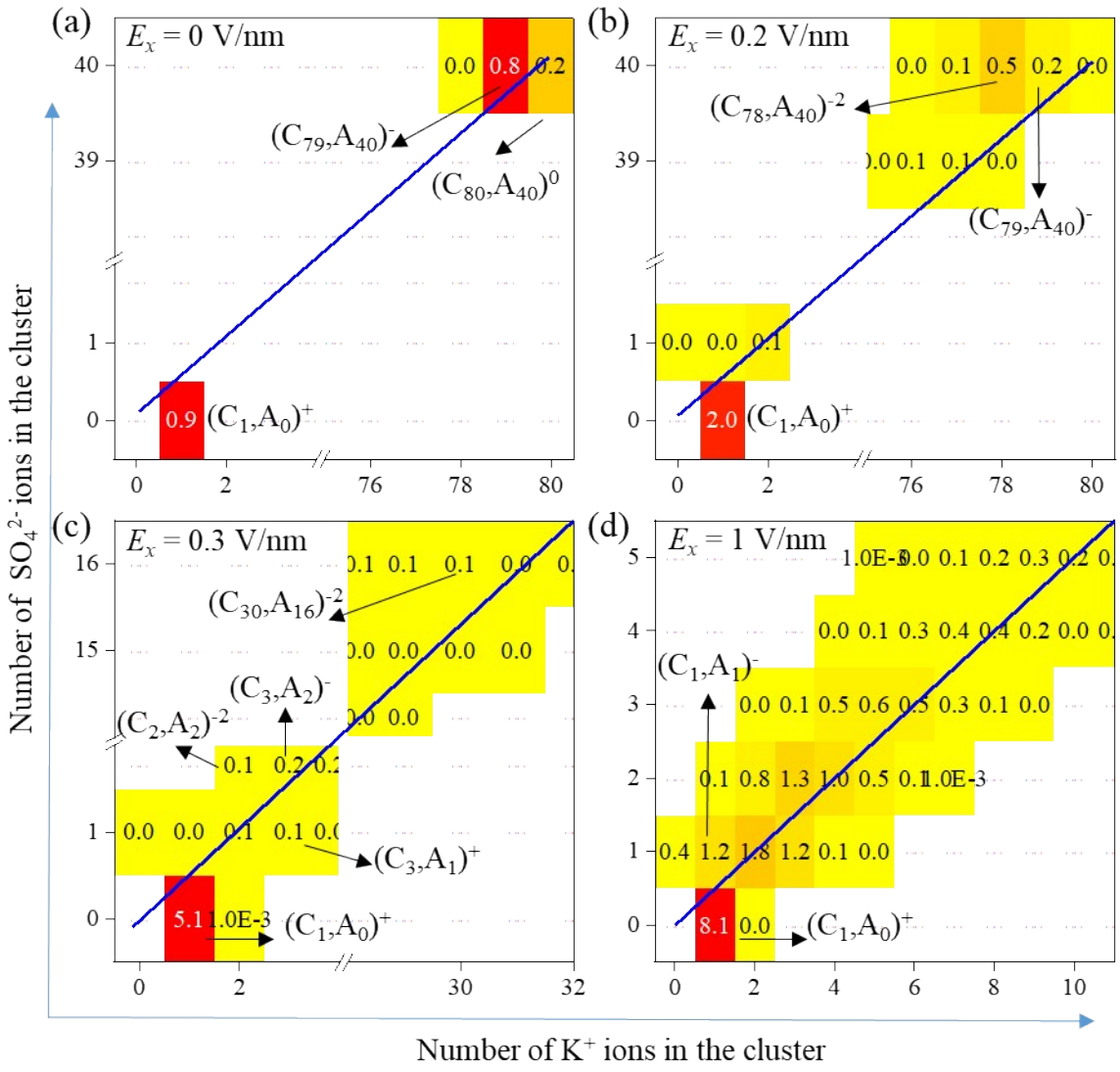


**Fig. S12.** Cluster distribution of the $K_2SO_4$ system as a function of electric field $E_x$ = (a) 0 V/nm, (b) 0.2 V/nm, (c) 0.3 V/nm, and (d) 1.0 V/nm, respectively. The symbol $(C_i, A_j)^{i-2j}$ represented a cluster comprising *i* Cations and *j* Anions with a charge of *i*-2*j*. The number in the figures indicated the average number of a given cluster per snapshot. The blue oblique line $i = 2j$ suggested the neutral clusters.

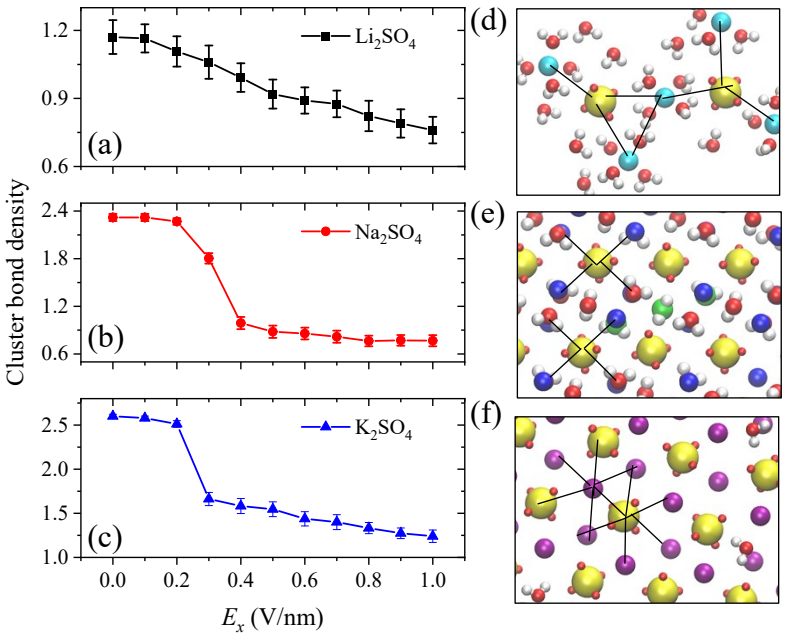


**Fig. S13.** Cluster bond density in aqueous of (a) $Li_2SO_4$, (b) $Na_2SO_4$ and (a) $K_2SO_4$ as the function of the electric field ($E_x$). (d-e) The ion associations within the $Li_2SO_4$ chain, $4Na{\cdot}2SO_4{\cdot}6H_2O$ hydrated salt, and $K_2SO_4$ ionic crystal in absence of electric field. Here, the associations between ions and water molecules were neglected. The cluster bond density of the $Li_2SO_4$ chain exceeded 1, primarily due to cation-cation associations.

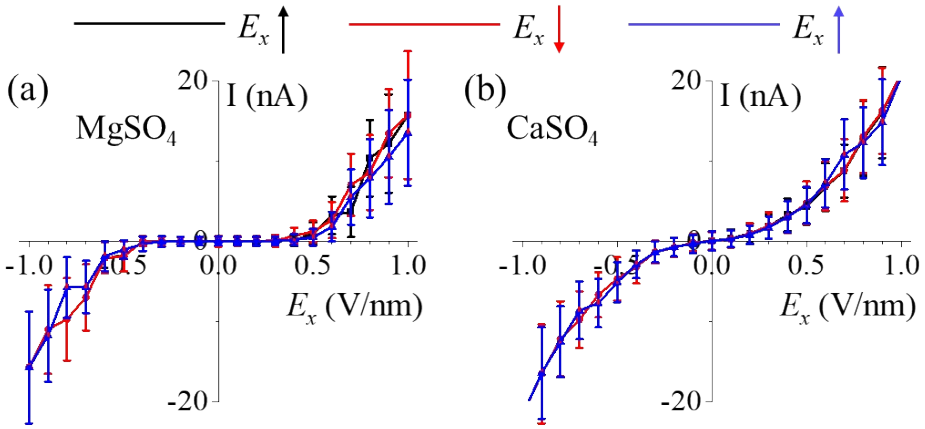


**Fig. S14.** The *I-V* characteristics of the electrolyte aqueous solutions in the angstrom-scale slit for (a) $MgSO_4$ and (b) $CaSO_4$.