Supporting Information

Ion Specificity at a Low Salt Concentration in Water-Methanol Mixtures Exemplified by a Growth of Polyelectrolyte Multilayer

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The classical Debye length (l_D) calculated according to Eq.4 in the main text might not be valid for the polyelectrolyte contained solutions. The effective Debye length ($l_{D\ eff}$) can be calculated by the following equation by taking the polyelectrolyte into account:[S1,S2]

$$l_{D\ eff}^{-1} = l_D^{-1}[1 + \frac{\sqrt{1000 N_A}\ln 3}{32\pi}(\frac{q^2}{\varepsilon_0 \varepsilon_r k_B T})^{3/2} \times \frac{(\sum_{i=1}^{n} c_i z_i^4)(\sum_{i=1}^{n} c_i z_i^2) - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} c_i c_j z_i^2 z_j^2 (z_j - z_i)^2}{(\sum_{i=1}^{n} c_i z_i^2)^{3/2}}] \qquad \text{(S1)}$$

where “i” and “j” are the different chemical species in the solution, c_i and z_i represent the molar concentration and charge of each specie “i”. N_A, q, ε_0, ε_r, k_B, and T are the Avogadro number, elementary charge, vacuum permittivity, dielectric constant of solvent, Boltzmann constant, and absolute temperature, respectively. In the present study, if we assume the absolute molar mass of the polyelectrolyte to be ~ 1×10^4 g mol^{-1} and the charge around the outer surface of the polyelectrolyte is 7 (like the biopolyelectrolyte, lysozyme), the effective Debye length is estimated to be ~ 5 nm in the presence 2 mM monovalent salt in water, which is smaller than that (~ 7 nm) calculated based on Eq. 4.

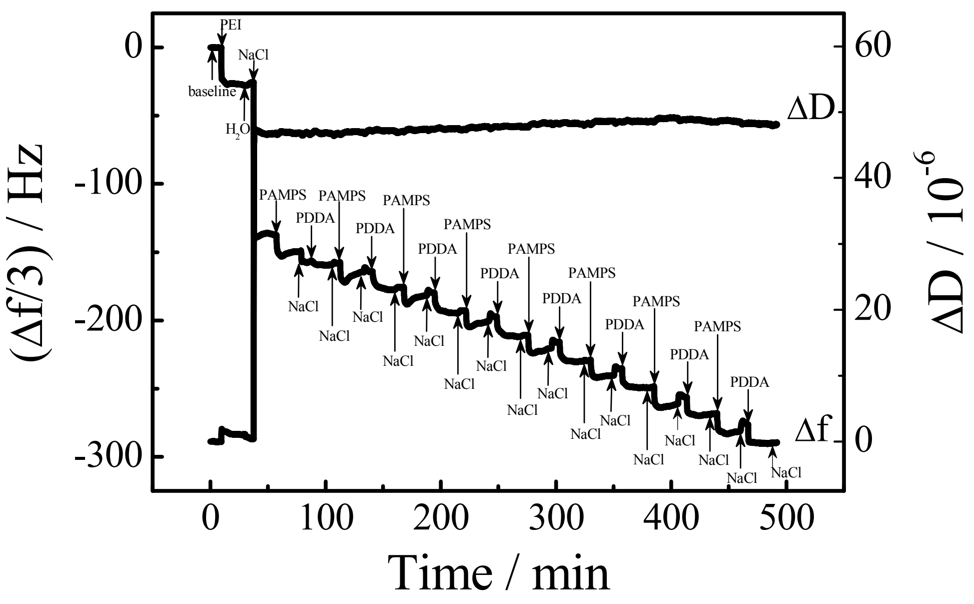

Figure S1. Changes in frequency (Δ*f*) and dissipation (Δ*D*) for the growth of PAMPS/PDDA multilayer in the presence of NaCl in the solvent mixture with the x_{M} of 25%, where the salt concentration is fixed 2.0 mM.

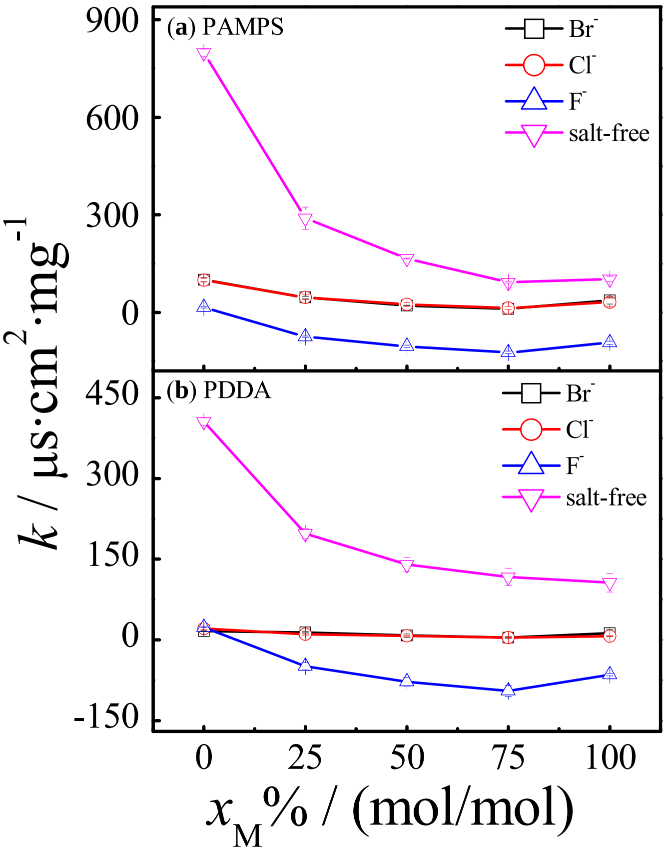

Figure S2. The change in conductivity (k) of PAMPS and PDDA as a function of the molar fraction of methanol (x_M) in the presence of different anions, where the polymer concentration is fixed at 0.1 mg mL^{-1} and the salt concentration is fixed at 2.0 mM. (a) PAMPS. (b) PDDA. The change of k in the salt-free solvent mixtures is also plotted in this figure for comparison. At the same x_M, the higher k in the salt-free solvent mixtures compared with that in the salts contained solvent mixtures, indicating that the added salts screen the charges on the polyelectrolyte chains and reduce the conductivity of polyelectrolytes. Similar results are also observed in the change of k in the presence of different cations (Figure S3). In addition, the change of k has a more obvious minimum at the x_M of 75% in the presence of salts, implying that the added salts might be favorable for the formation of solvent complexes.[S3,S4]

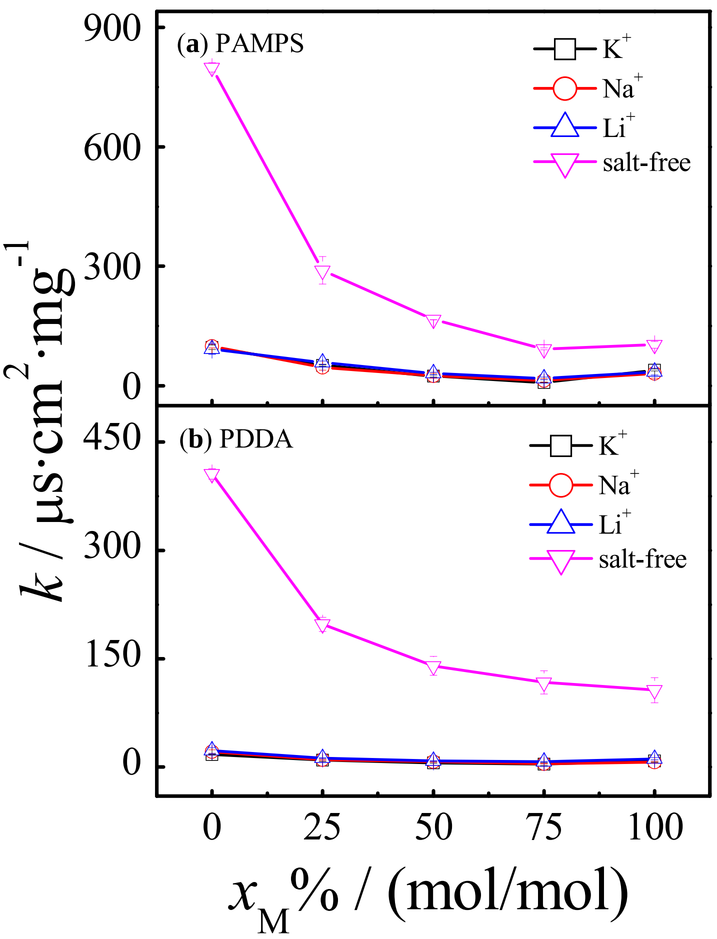

Figure S3. The change in conductivity (k) of PAMPS and PDDA as a function of the molar fraction of methanol (x_M) in the presence of different cations, where the polymer concentration is fixed at 0.1 mg mL^{-1} and the salt concentration is fixed at 2.0 mM. (a) PAMPS. (b) PDDA. The change of k in the salt-free solvent mixtures is also plotted in this figure for comparison.

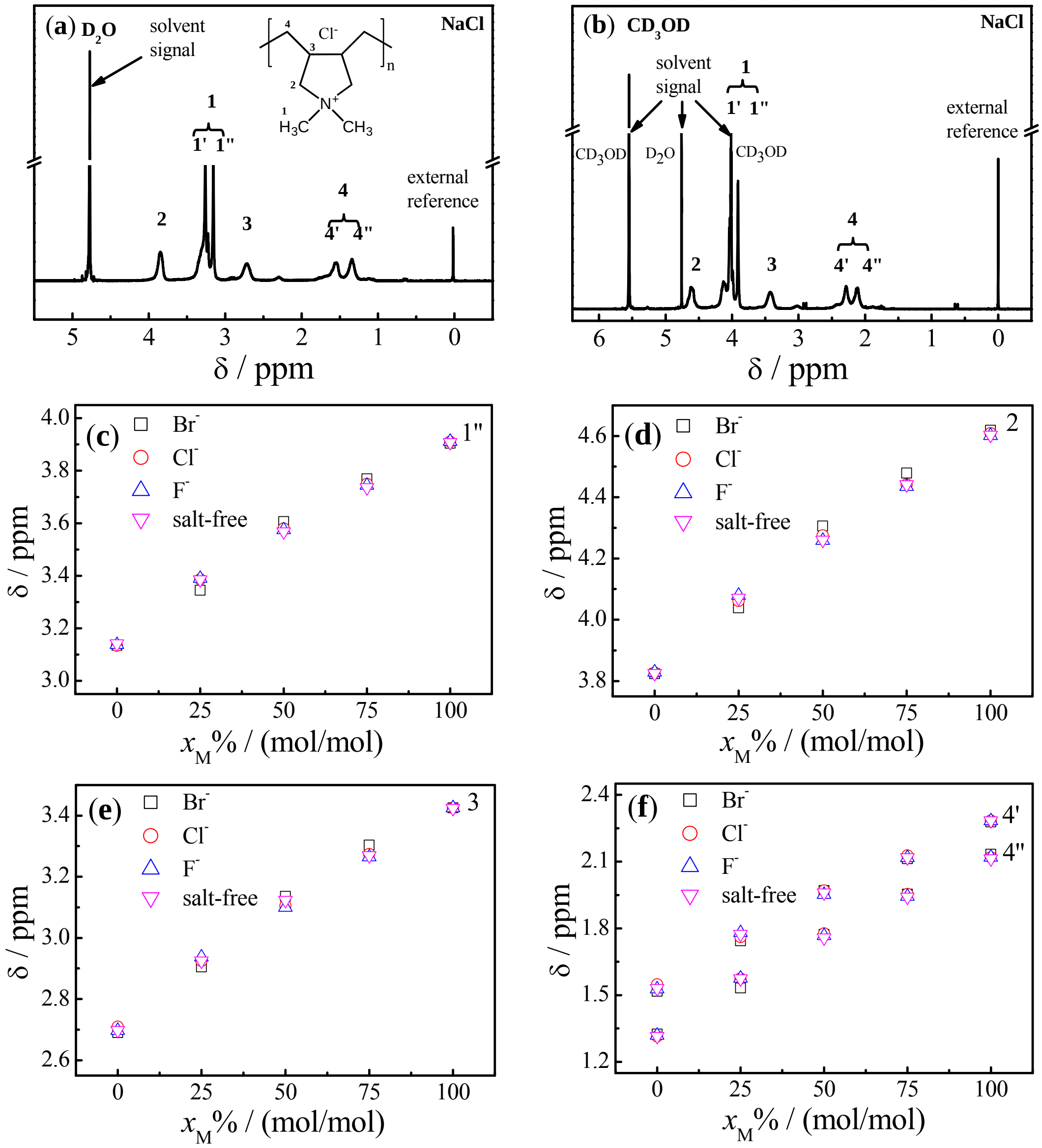

Figure S4. H^1NMR spectra of PDDA in the D_2O-CD_3OD mixtures in the presence of different anions. (a) The H^1NMR spectrum of PDDA in D_2O in the presence of 2.0 mM NaCl, where the assignments for the signals are labeled on the chemical structure of PDDA. (b) The H^1NMR spectrum of PDDA in CD_3OD in the presence of 2.0 mM NaCl, where the assignments for the signals can be found in (a). (c), (d), (e), and (f) show the change in chemical shift (δ) as a function of the molar fraction of deuterated methanol (x_M) for the resonance peaks 1, 2, 3, and 4, respectively. Only the change in δ for the resonance peak 1″ is shown in (c) as the resonance peak 1′ is overlapped with the solvent signal of CD_3OD. The change of δ in the salt-free solvent mixtures is also plotted in this figure for comparison. For all the resonance peaks, the increase of δ with the x_M is attributed to the increasing methanol effect on the chemical shift.[S5,S6] No obvious specific anion effect can be observed in the change of δ in the whole range of x_M from 0% to 100%.

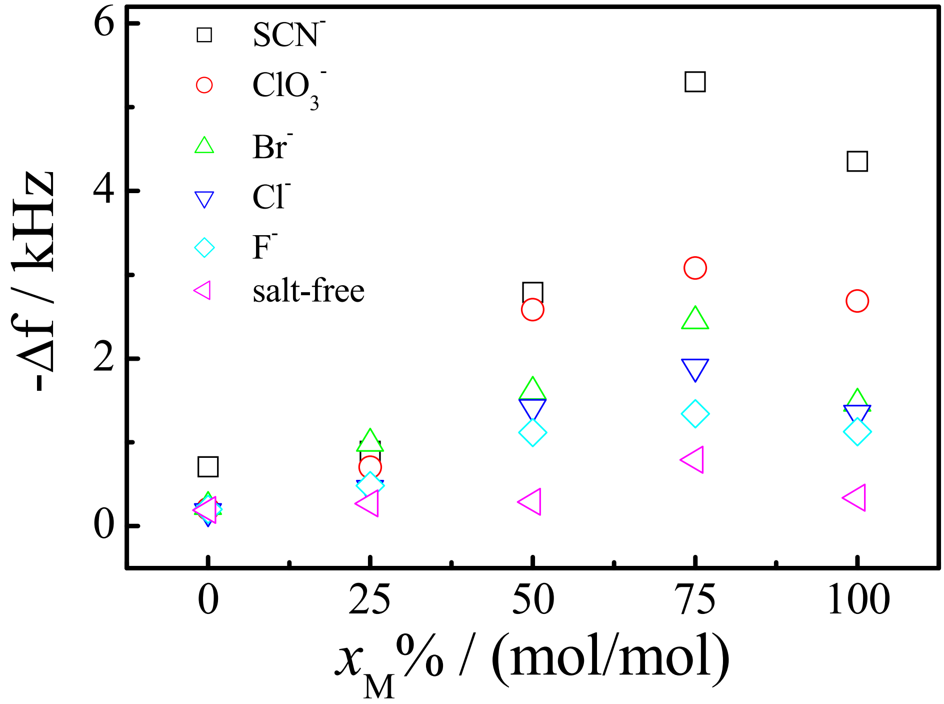

Figure S5. The change in frequency (–Δ*f*) for the 8-bilayer PAMPS/PDDA multilayer as a function of the molar fraction of methanol (x_M) in the presence of different anions, where the salt concentration is fixed at 2.0 mM. The –Δ*f* in the salt-free solvent mixtures is also plotted in this figure for comparison. Obviously, the addition of salts to the solvent mixtures is favorable for the multilayer growth because the added salts lead the polyelectrolyte chains to adopt a more coiled conformation.

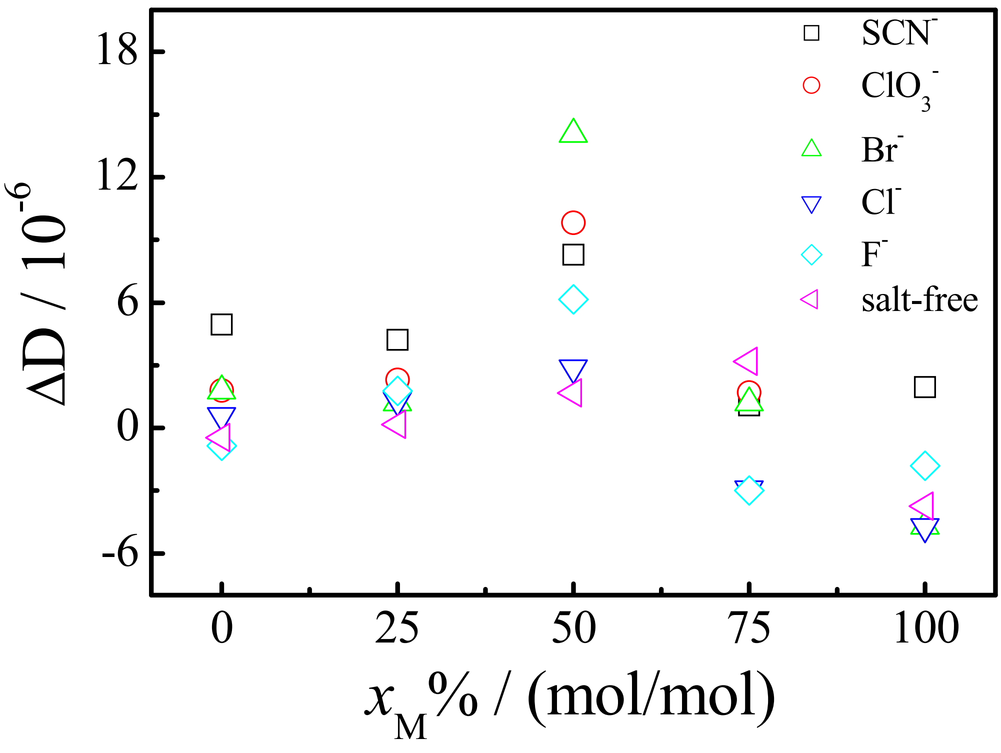

Figure S6. The change in dissipation (Δ*D*) for the 8-bilayer PAMPS/PDDA multilayer as a function of the molar fraction of methanol (x_M) in the presence of different anions, where the salt concentration is fixed at 2.0 mM. The Δ*D* in the salt-free solvent mixtures is also plotted in this figure for comparison. Obviously, Δ*D* in the salt-free solvent mixtures has a similar change with that in the salts contained solvent mixtures.

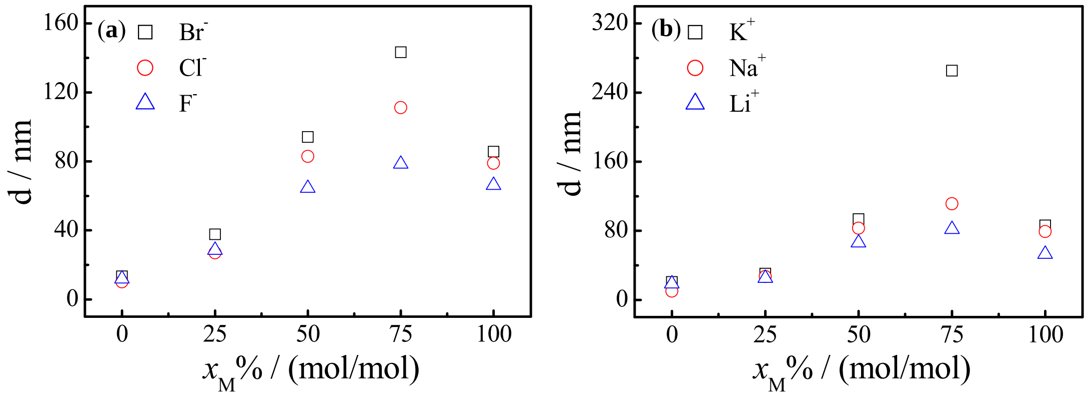

Figure S7. The change in thickness (*d*) for the 8-bilayer PAMPS/PDDA multilayer as a function of the molar fraction of methanol (x_M) in the presence of different ions, where the salt concentration is fixed at 2.0 mM. (a) For the anions. (b) For the cations. Considering the small values of ΔD (see text), the thickness of the PEM estimated by the Sauerbrey equation may not lead to a large error. The density of the multilayer film is evaluated to be ~1000 kg m^{-3} during the calculation.

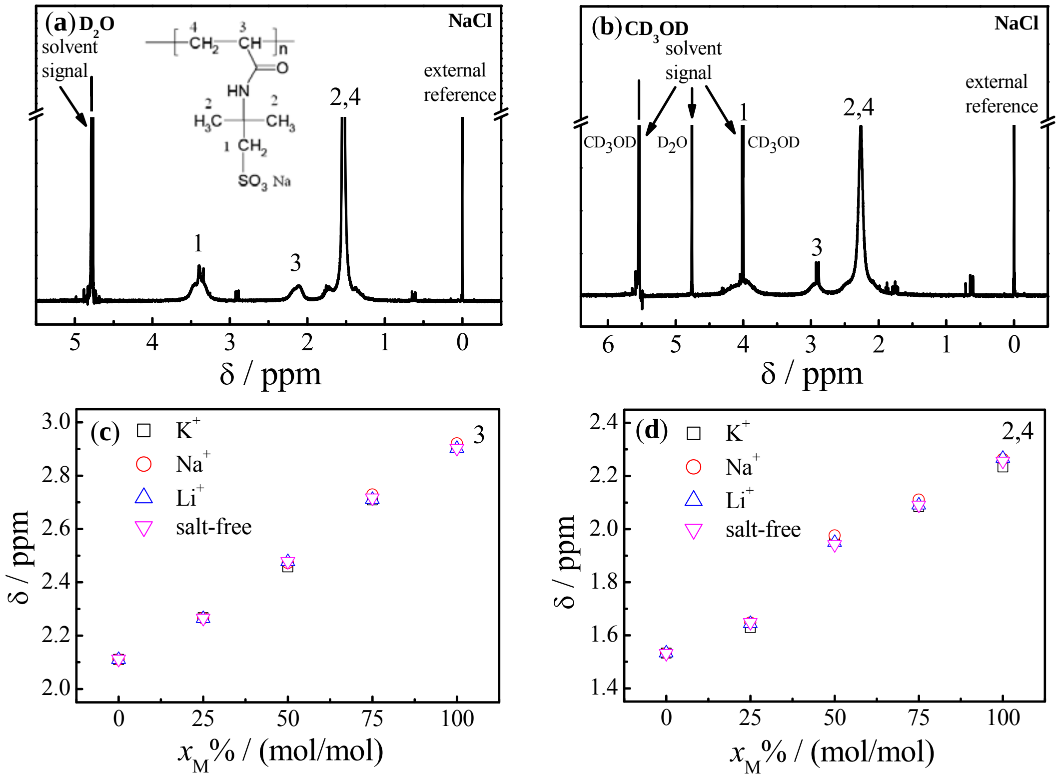

Figure S8. The H^{1}NMR spectra of PAMPS in the D_2O-CD_3OD mixtures in the presence of different cations. (a) The H^{1}NMR spectrum of PAMPS in D_2O in the presence of 2.0 mM NaCl, where the assignments for the signals are labeled on the chemical structure of PAMPS. (b) The H^{1}NMR spectrum of PAMPS in CD_3OD in the presence of 2.0 mM NaCl, where the assignments for the signals can be found in (a). (c) The change in chemical shift (δ) as a function of the molar fraction of deuterated methanol (x_M) for the resonance peak 3 in the presence of different cations. (d) The change in chemical shift (δ) as a function of the molar fraction of deuterated methanol (x_M) for the resonance peaks 2 and 4 in the presence of different cations. The change in δ for the resonance peak 1 is not shown as the peak is overlapped with the solvent signal of CD_3OD. The change of δ in the salt-free solvent mixtures is also plotted in this figure for comparison. The gradual increase of δ for all the resonance peaks with the x_M is attributed to the increasing methanol effect on the chemical shift.[S5,S6] No obvious specific cation effect can be observed in the change of δ in the whole range of x_M from 0% to 100%.

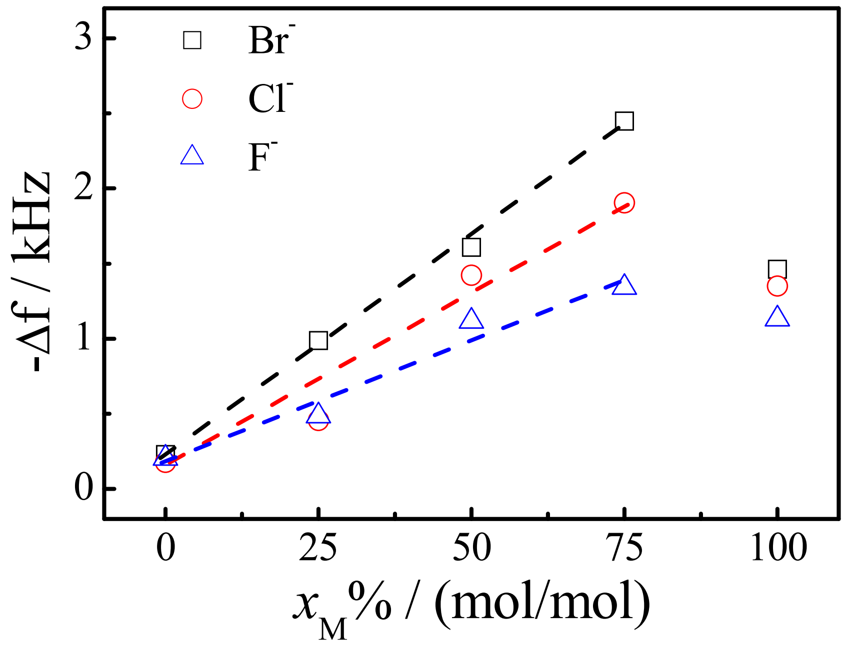

Figure S9. The frequency shifts (Δf) for NaBr, NaCl, and NaF have an almost linear relationship with the molar fraction of methanol (x_M) between 0% and 75%.

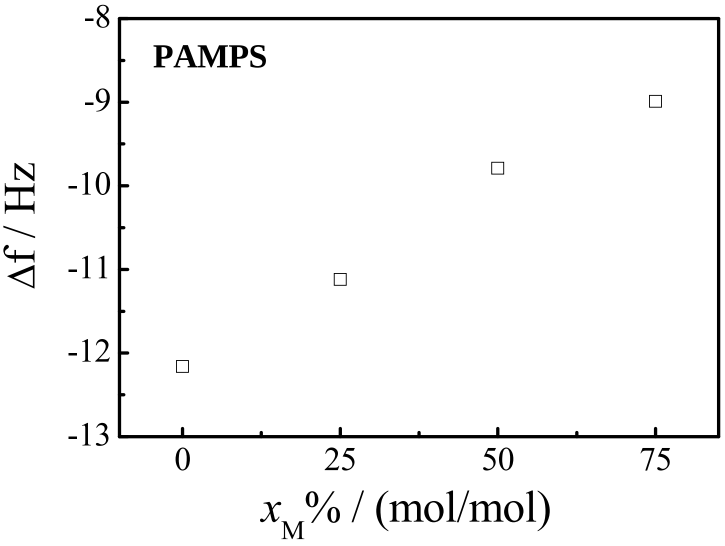

Figure S10. The frequency change (Δf) of a thin PAMPS layer adsorbed on a SiO_2 coated resonator surface as a function of the molar fraction of methanol (x_M). Here, the Δf is obtained by taking the blank resonator as a reference. The increase of Δf with the x_M from 0% to 75% indicates the gradual desolvation and collapse of polyelectrolyte due to the decrease of solvent quality.

References

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