

Supporting Information

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Ligand-Binding Mediated Gradual Ionic Transport in
Nanopores

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Supplementary Methods

Effect of increasing Ca^{2+} ion presence on the electrostatic layer thickness on the ITO/glass substrate.

To verify that the changes in peak current densities shown in Figure 2 are not related to the electrostatic layer thickness change on the ITO surface upon Ca^{2+} addition, the effect of Ca^{2+} addition on the CV curves from the ITO/glass substrate without any silica film on top were tested (Figure S5). There was no connection between Ca^{2+} amount and the peak current density ($i_{p,a}$) at different scan rates from the CV measurements of ITO/glass substrate both at high and low pH conditions. Since the electrolyte concentration of KCl (100mM) is significantly higher than the maximum concentration of Ca^{2+} ions used in this study (5mM), the Ca^{2+} ion presence effect on the charged pore layer thickness is negligible compared to the effect originated by the presence of KCl.

Verifying mesoporous film stability upon long electrolyte / mesoporous film interactions

The possible defects in the films due to the long interaction of our porous films with electrolytes were tested at pH=3 and pH=10. Therefore, the PMEP functional films were incubated inside both pH=3 and pH=10 electrolyte solutions with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and compared the film thickness and free pore volume to those reported before incubation by using Ellipsometry (Figure S6a). As shown in Figure S6, SEM images showed no significant defects (e.g., micron-sized cracks), and ellipsometry did not present any significant mesoporous film thickness or pore size variations.

Supplementary Figures

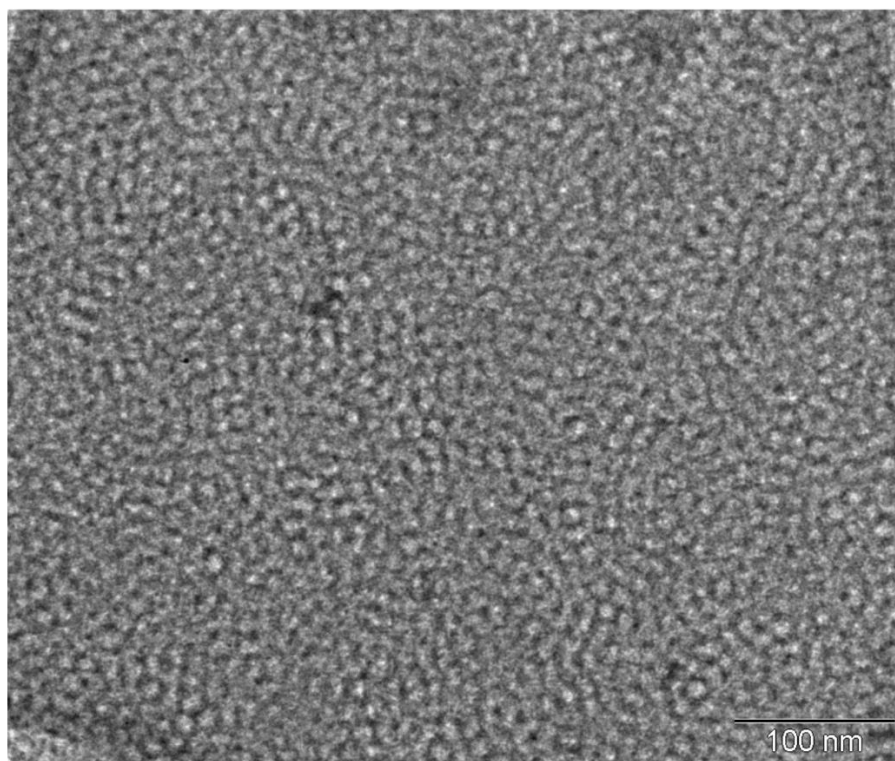


Figure S1. TEM micrograph of the mesoporous silica film used in this work.

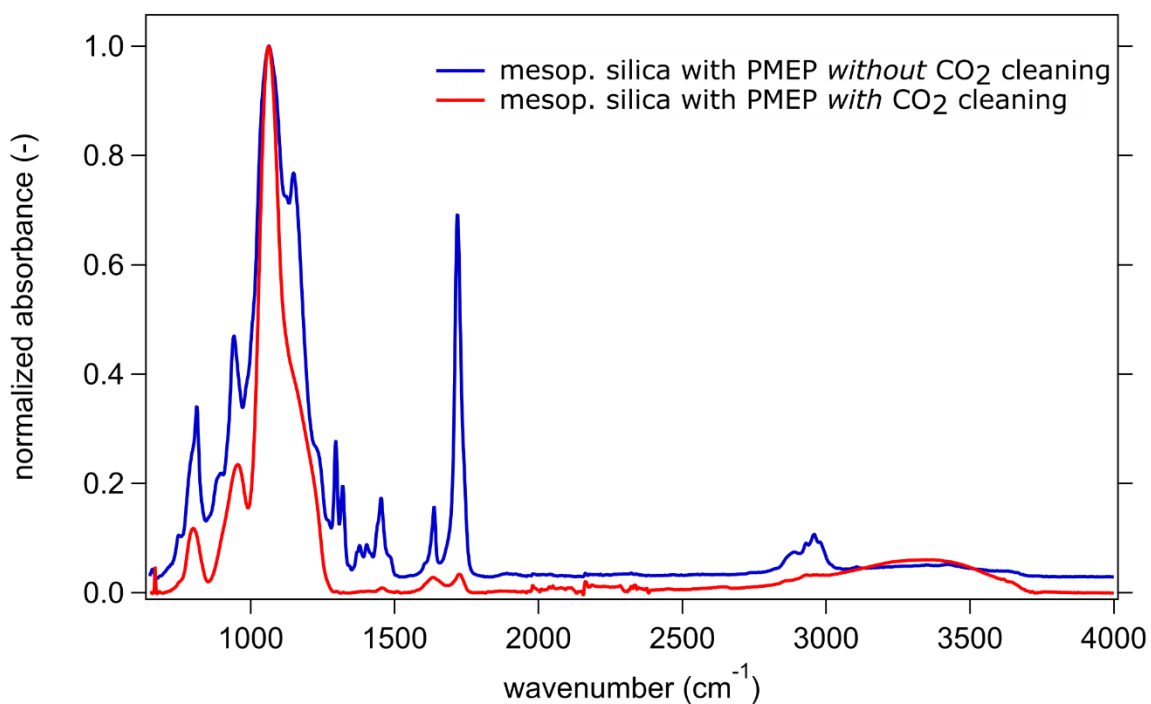


Figure S2. ATR-IR results of the PMEPP functionalized mesoporous films with (red) or without (blue) CO₂ plasma cleaning of the photo-iniferter molecules prior to the photopolymerization. Both spectra were baseline corrected and normalized to the at 1065 cm⁻¹ from the Si-O-Si vibration.

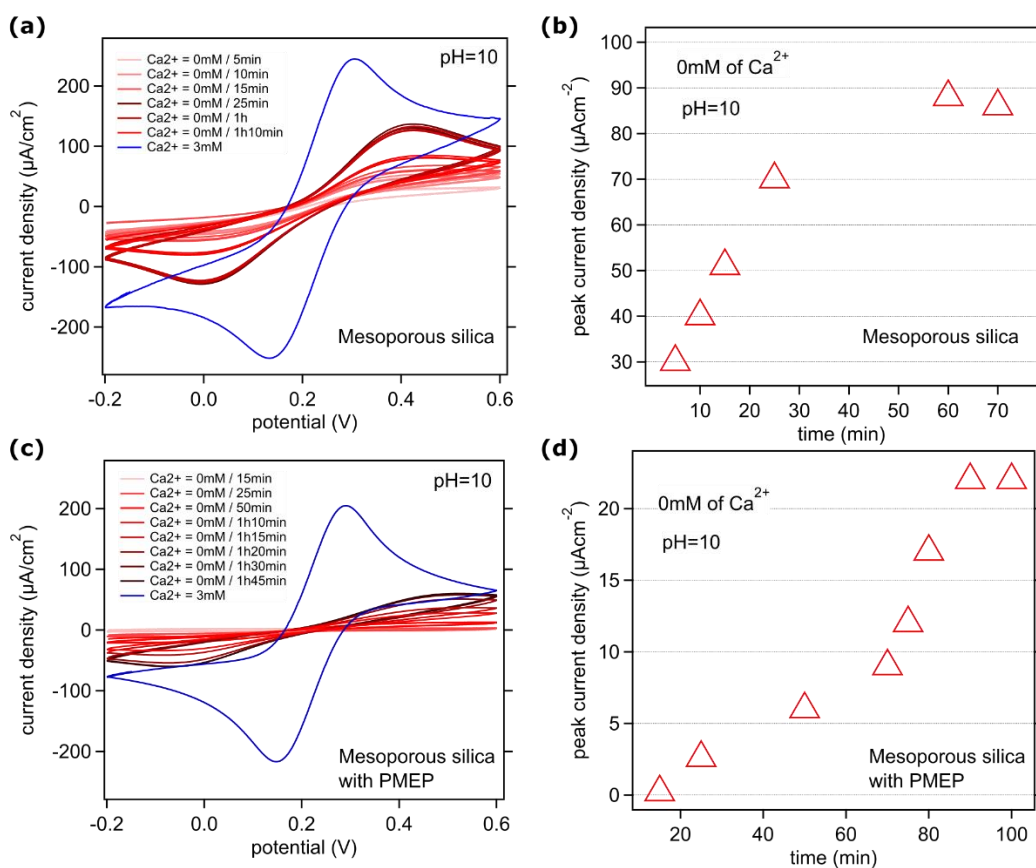


Figure S3. (a,c) Cyclic voltammograms collected at increasing interaction periods of electrolytes with membranes (a) without and (c) with PMEP pore functionalization. The pH of the electrolyte solutions was fixed at pH=10, and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used as an ionic probe. All the CV measurements were performed by including 0 mM Ca^{2+} inside the electrolyte solution except the blue curves ($\text{Ca}^{2+}=3\text{mM}$). Different shades of red-colored CV curves identify the measurement done at different membrane – electrolyte interaction times. Scan rate = 200 mV/s. (b,d) Average peak current density as a factor of increasing electrolyte and membrane interaction times obtained from the CV curves of (b) non-functional and (d) PMEP functional silica pores.

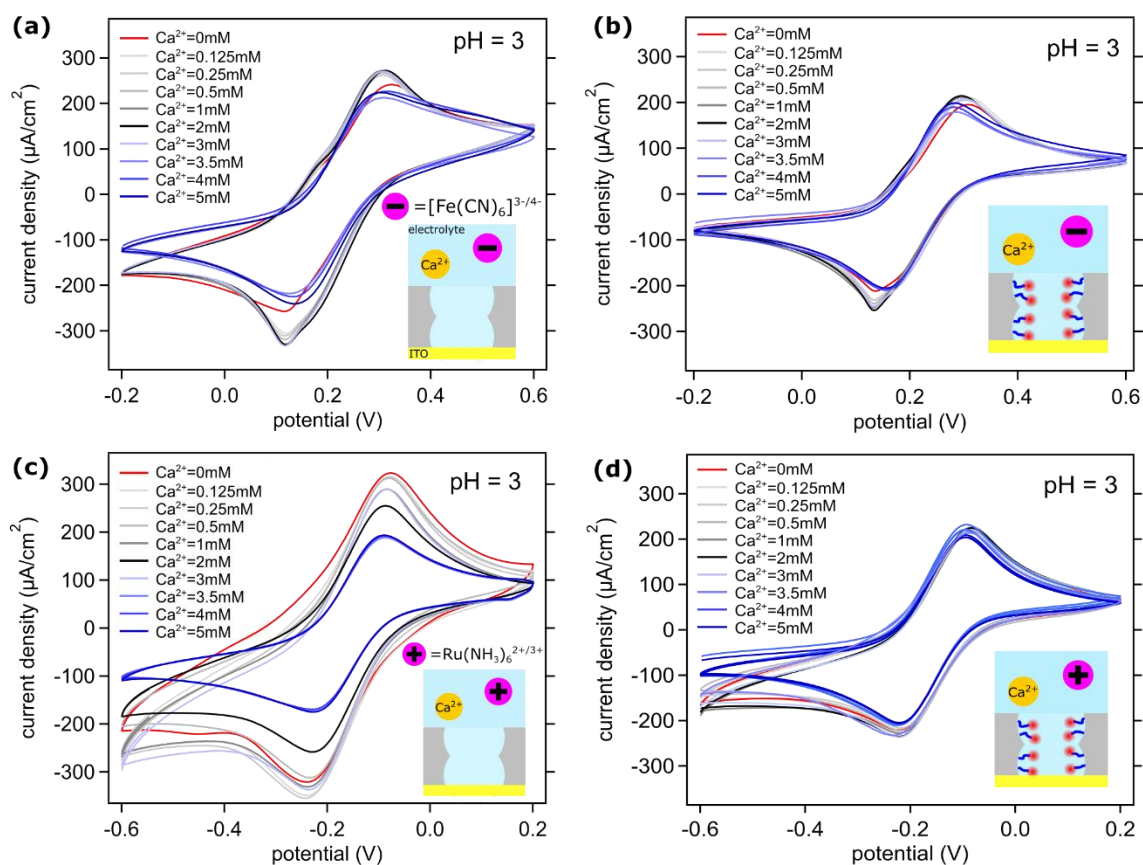


Figure S4. Cyclic voltammograms were collected from the measurements of our mesoporous silica films (a,c) before and (b,d) after PMEP modification after the electrolytes were loaded with various amounts of CaCl_2 inside. The pH of the electrolyte solutions was fixed at pH 3. We used (a,b) $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and (c,d) $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ as the anionic and cationic probes, respectively. Scan rate = 200 mV/s. Insets illustrate the measured materials and ingredients in the electrolytes.

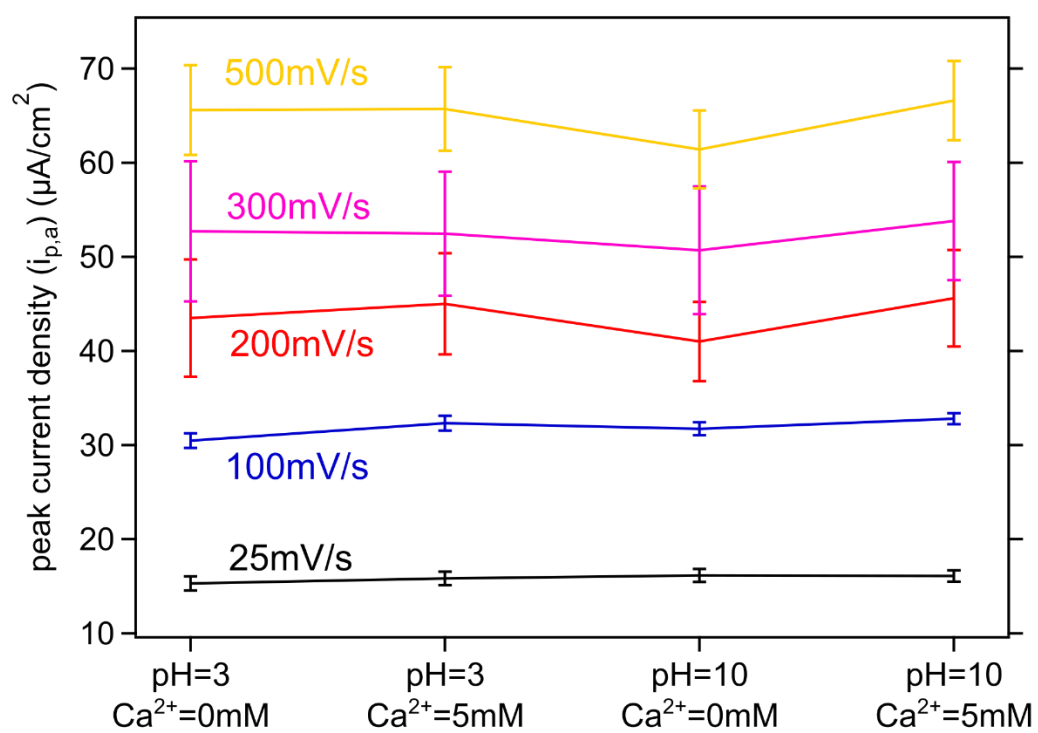


Figure S5. Peak current density, scan rate (different colors), pH (3 or 10), and Ca^{2+} amount (0 mM and 5 mM) relation quantified from the CV measurements of our unmodified ITO/glass substrate (no mesoporous film). Error bars are sd.

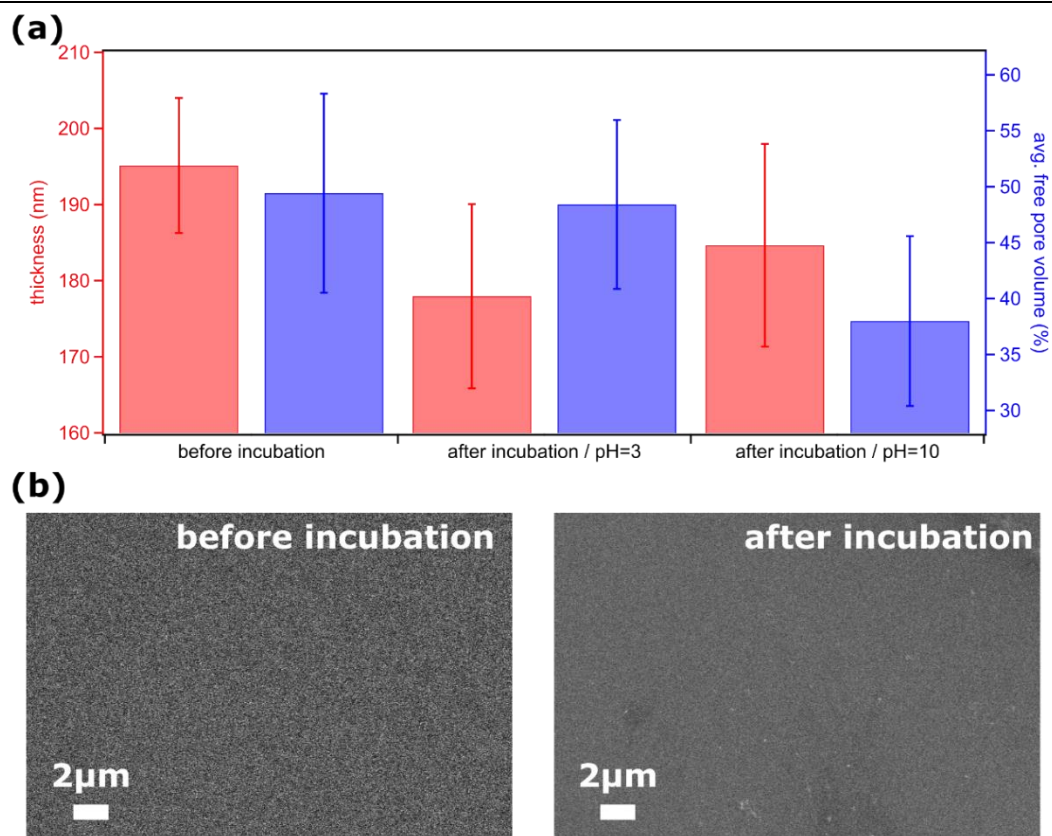


Figure S6. Results from ellipsometer measurements of mesoporous silica films with PMEP at their pores before and after incubating the films inside the electrolyte solutions with low (pH=3) and high (pH=10) pH. SEM image showing the mesoporous films with PMEP before and after (inside of electrolyte having pH=10 during 200 min) the incubation. Incubation periods of films inside pH3 and pH10 solutions are 370 min and 200 min, respectively. A stable film thickness in the range of 175-195 nm and absence of crack formation at the surface is observed.

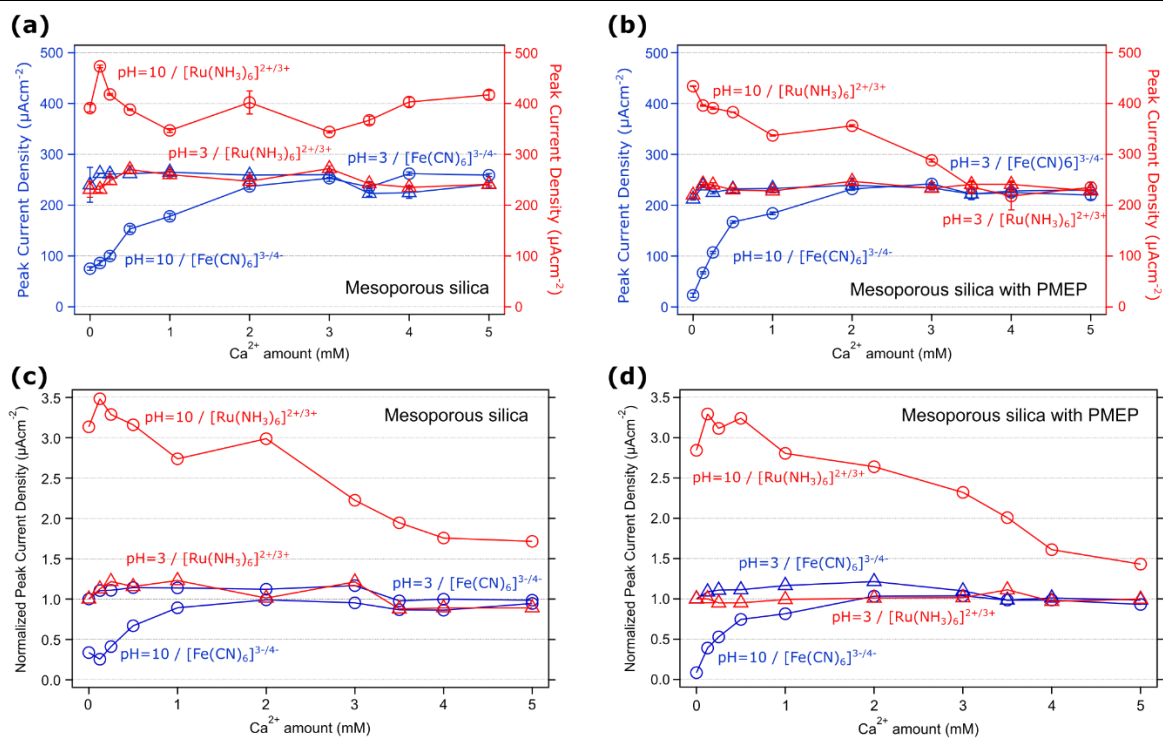


Figure S7. (a-b) *Non-normalized* peak current density and Ca^{2+} amount relation collected from the CV measurements of (a) mesoporous silica film and (b) mesoporous silica film after PMEP pore functionalization. The *normalized* peak current density of the data (a) and (b) are presented in Figures 3a and 3b, respectively. (c-d) Calculated normalized peak cathodic current density ($i_{p,c}$) and Ca^{2+} ion amount relation are shown for the mesoporous silica film (c) without and (d) with PMEP pore functionalization. The presented $i_{p,a}$, $i_{p,c}$ data in this Figure and Figure 3 were determined from the same CV measurements of the films. Error bars are sd.

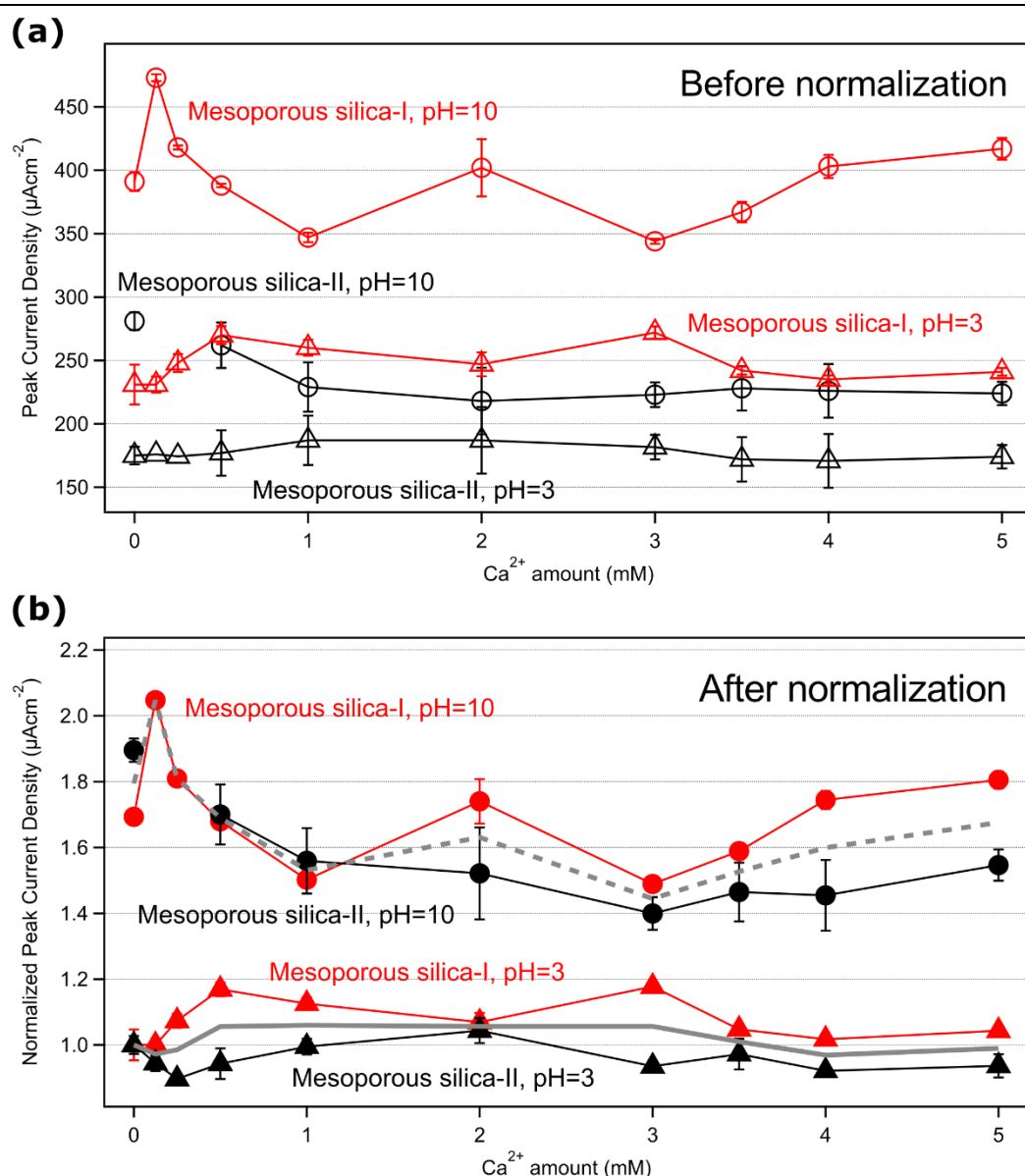


Figure S8. (a) Non-normalized and (b) normalized peak current densities calculated from the CV measurements of mesoporous silica films having different thicknesses and free pore volume. Mesoporous Silica-I (red) is 228.7 ± 7.8 nm thick and $V_{free,pore} = 48 \pm 2.0\%$. Mesoporous Silica-II (black) has 191 ± 9.6 nm thickness and $V_{free,pore} = 55 \pm 2.5\%$. Their electrochemical transport behaviours were calculated by using $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ as an ionic probe and after fixing the pH of the electrolytes at pH=10 (empty and filled circles) and pH=3 (empty and filled triangles). In (b) the grey dashed and straight lines show the average $i_{p,a}$ from the data presented by filled circles (pH=10) and by filled triangles (pH=3), respectively.

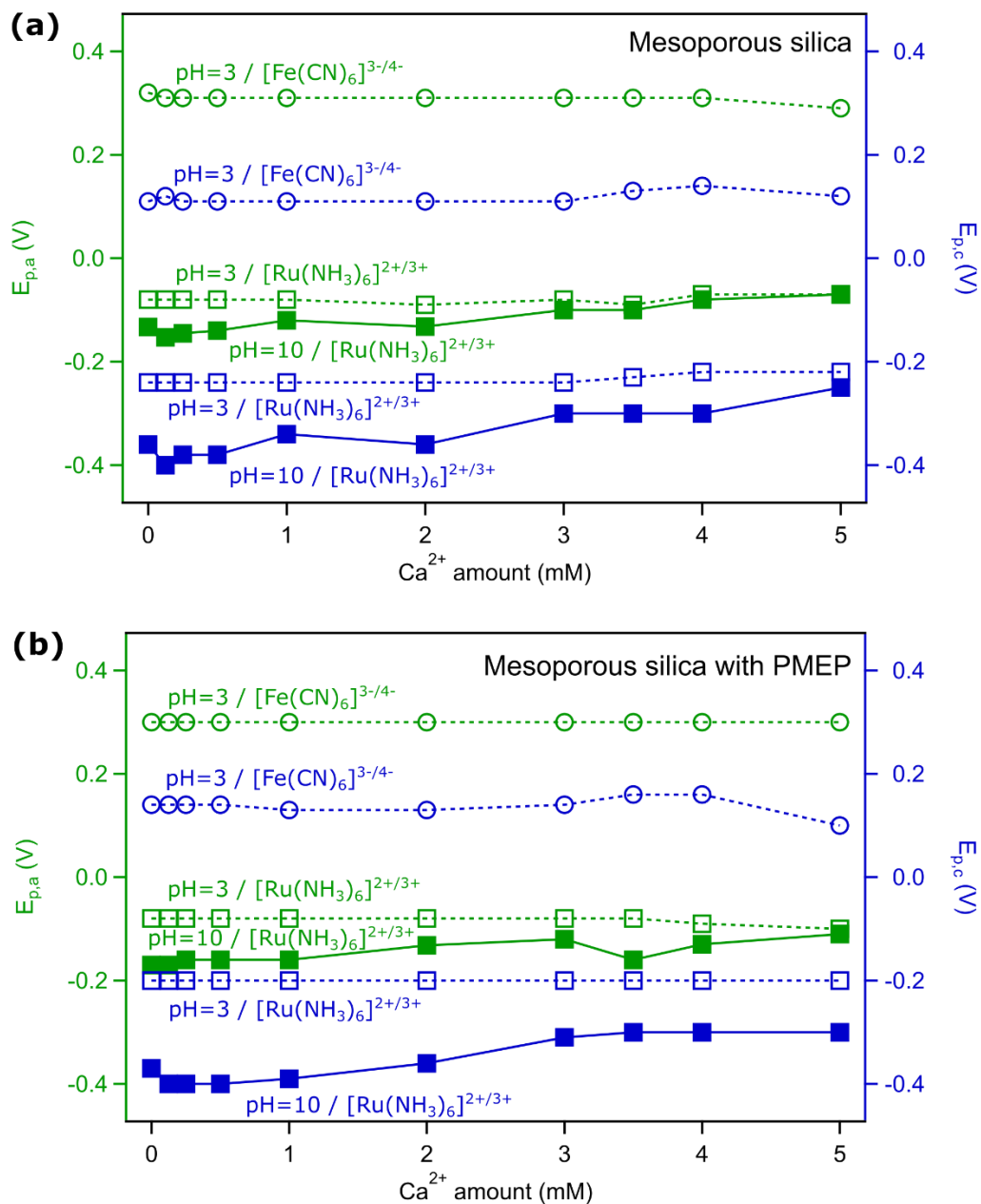


Figure S9. Graphs showing the changes in the potential values where the peak currents appear in the oxidation ($E_{p,a}$) and reduction ($E_{p,c}$) parts of the CV curves collected from the measurements of (a) mesoporous silica without and (b) with PMEP pore functionalization. Peak splitting (or peak-to-peak potential difference, ΔE_p) is calculated as $\Delta E_p = E_{p,a} - E_{p,c}$. Electrolytes had different pH (filled markers \rightarrow pH=10; empty markers \rightarrow pH=3), different Ca^{2+} ion concentrations, and ionic probes as $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (circle shape markers, abbreviation Fe) or $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ (empty box shape markers, abbreviation Ru) type ionic probes.

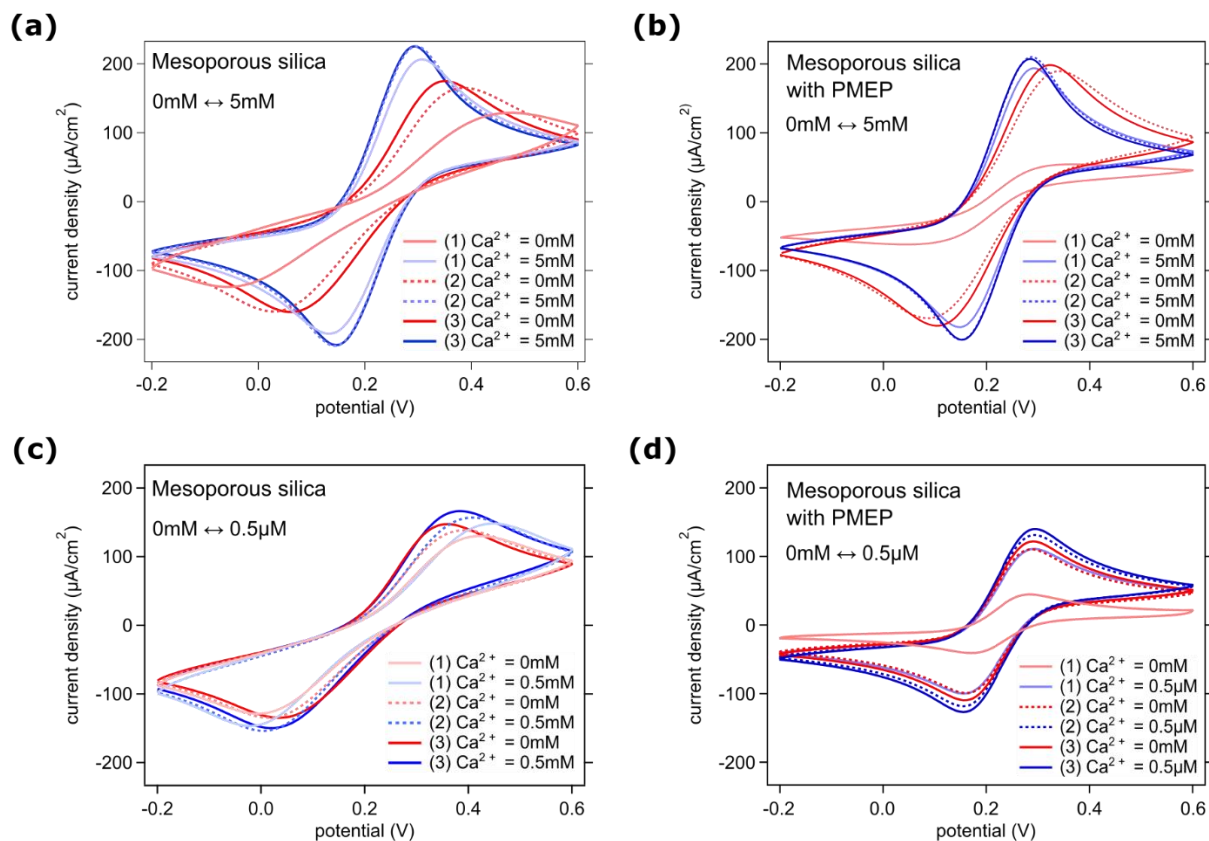


Figure S10. Cyclic voltammograms present the transport of anionic redox probes ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) as a factor of reversibility of Ca^{2+} ion adsorption /desorption on mesoporous silica films (a) before and (b) after PMEP pore functionalization when the electrolyte is loaded with 5 mM (blue curves) and 0 mM (red curves) of CaCl_2 . (c,d) In similar meanings, the reversibility of the same membranes was also tested by dissolving a tiny amount (0.5 μM) of CaCl_2 in the electrolyte solution in contact with our mesoporous silica membranes (c) before and (d) after pore functionalization. The numbers in parathesis in each Figure annotation present the loading sequence with 0 mM, 5 mM or 0.5 μM Ca^{2+} ion included solutions. For instance, “(2) $\text{Ca}^{2+} = 0.5 \mu\text{M}$ ” stands for the second round of filling the pores with electrolyte including 0.5 μM Ca^{2+} inside.

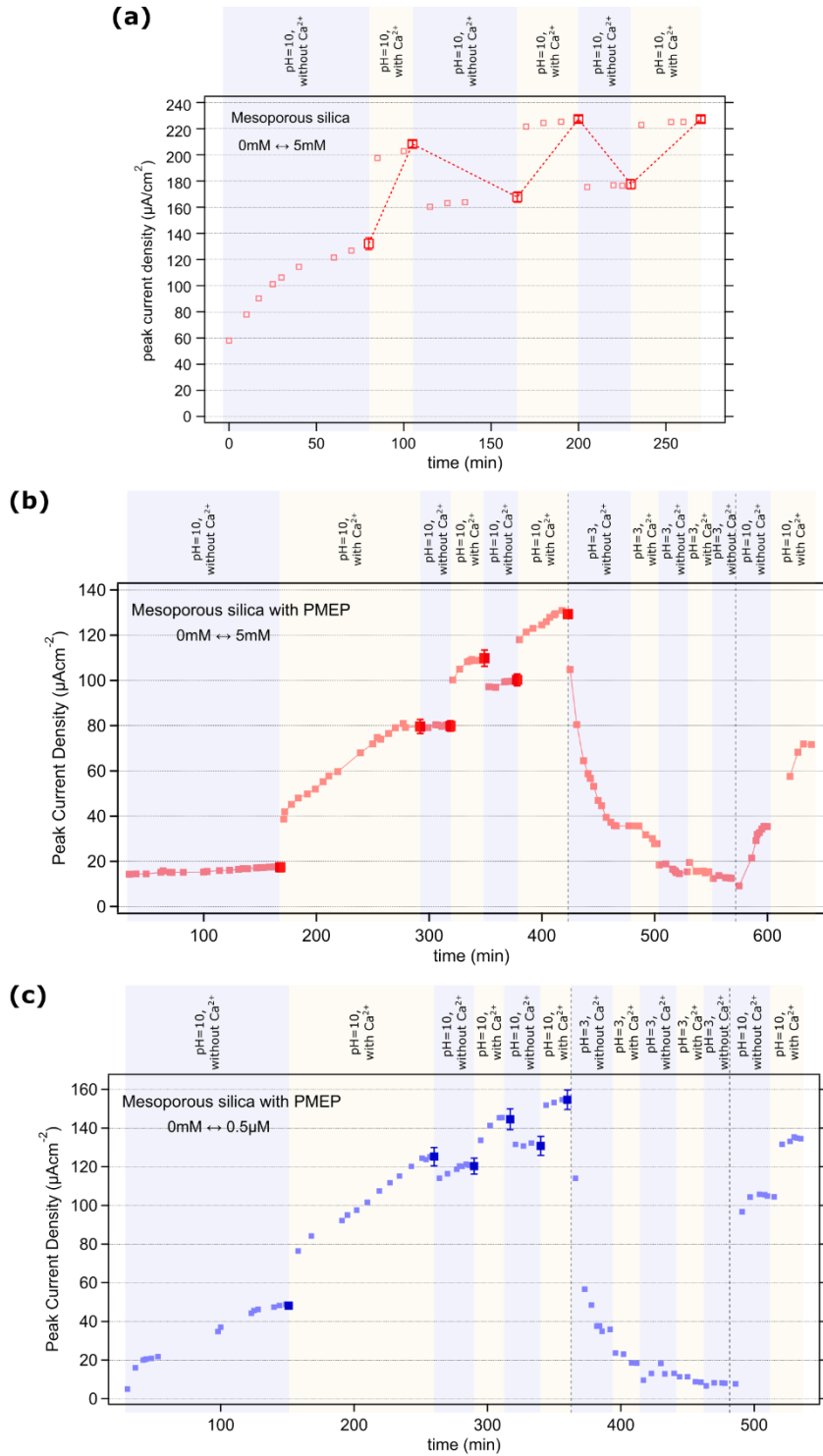


Figure S11. Peak current density values of mesoporous silica films (a) without and (b-c) with PMEP pore functionalization as a factor of changing film-electrolyte interaction times at different Ca²⁺ ion loading cycles (5 mM, 0.5 μM, or 0 mM of CaCl₂) and (b-c) pH. The pH of electrolytes was fixed at pH=10 for (a) and at pH=10 and pH=3 for (b-c). The blue and orange shaded areas indicate the absence and presence of Ca²⁺ inside the electrolyte, respectively, and the borders of these shed areas indicate the contact period of these electrodes with our films. An anionic redox probe ([Fe(CN)₆]^{3-/4-}) was used for all the CV experiments. (a-c) Faded (small size) markers show the peak current densities before $i_{p,a}$ data reaching a plateau. Data shown by large and darker filled boxes represent the measurements after the peak current density reached a plateau, and they are identical to those presented in Figure 4. Error bars are only shown for the dark data points, and they are sd.

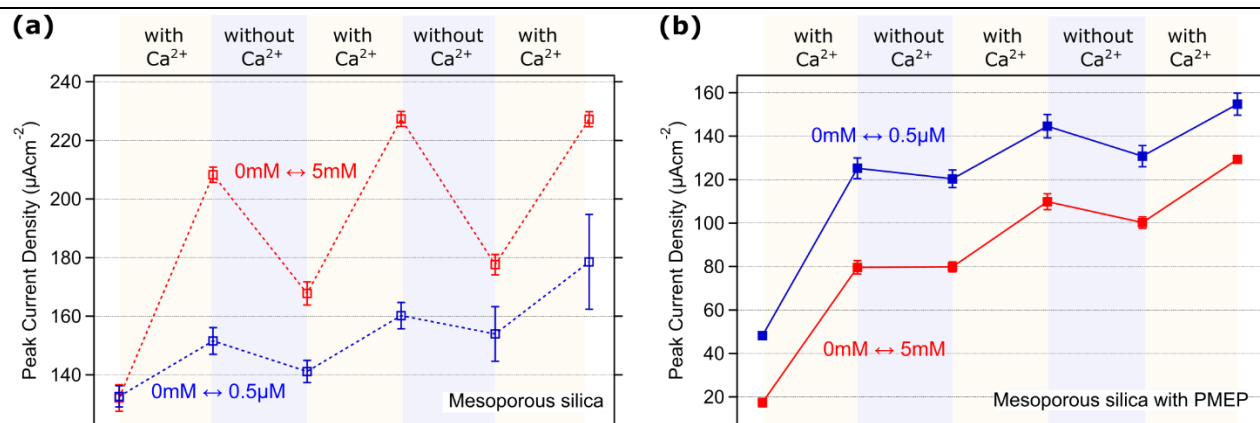


Figure S12. (a) Non-normalized (normalized data presented in Figure 4a,b) peak current density relation with loading/unloading of the nanopores (a) without and (b) with PMEP by Ca^{2+} ions. To this direction, we did the reversibility studies by using electrolytes including 0mM or 5 mM Ca^{2+} ions (red) or 0 mM and 0.5 μM Ca^{2+} (blue). ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) used as an ionic redox probe, and the solution pH was fixed at pH=10. Different color shaded areas indicate if the electrolyte has Ca^{2+} ions (orange) inside or not (blue) and indicate the time interval of these electrolytes in contact with our films. Error bars are sd.

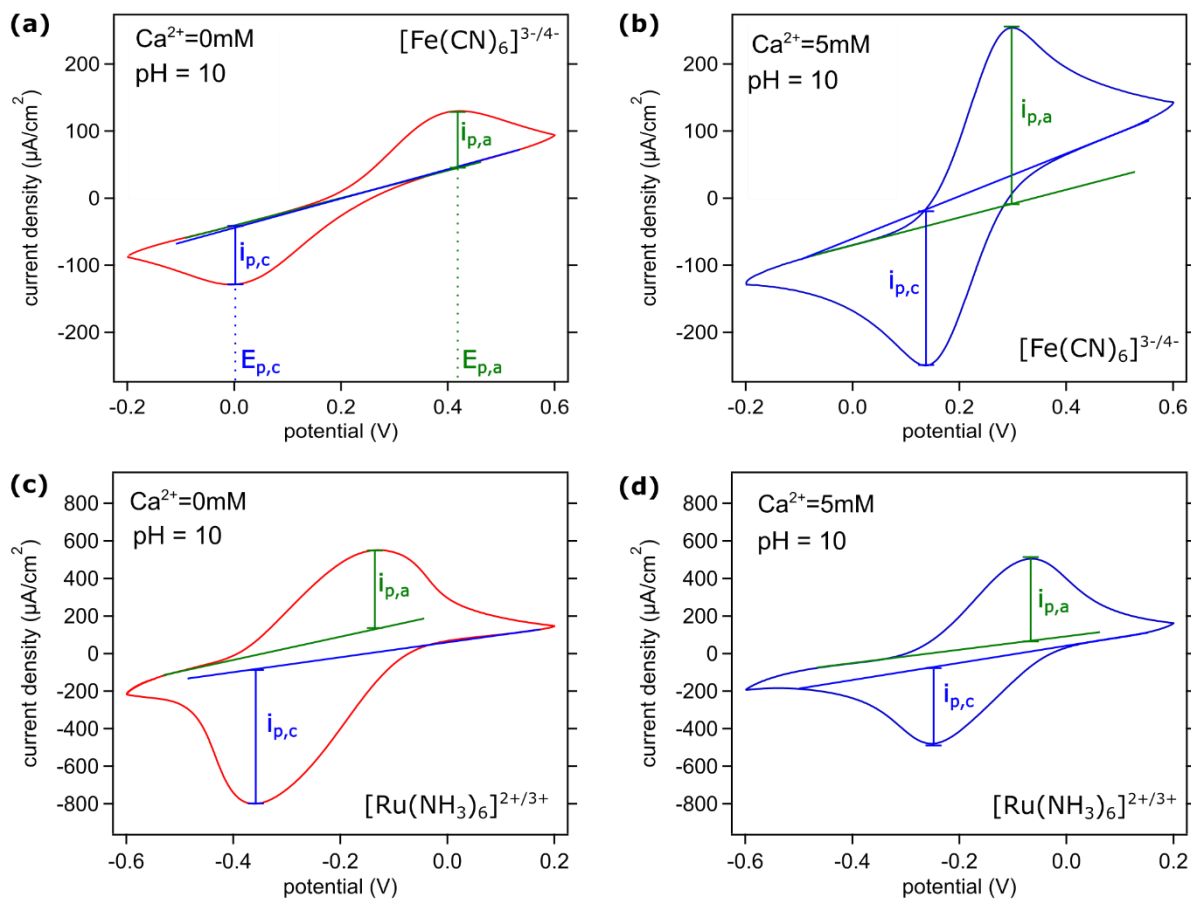


Figure S13. The method for obtaining the anodic current ($i_{p,a}$) and cathodic current ($i_{p,c}$) peaks from different CV curves collected while using (a-b) $[\text{Fe}(\text{CN})_6]^{3-/4-}$ or (c-d) $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ as ionic probes inside of electrolyte solution containing (a,c; red) 0 mM or (b,d; blue) 5 mM Ca^{2+} ions inside ($\text{pH}=10$). The potential values where the anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peaks were observed are shown in (a).

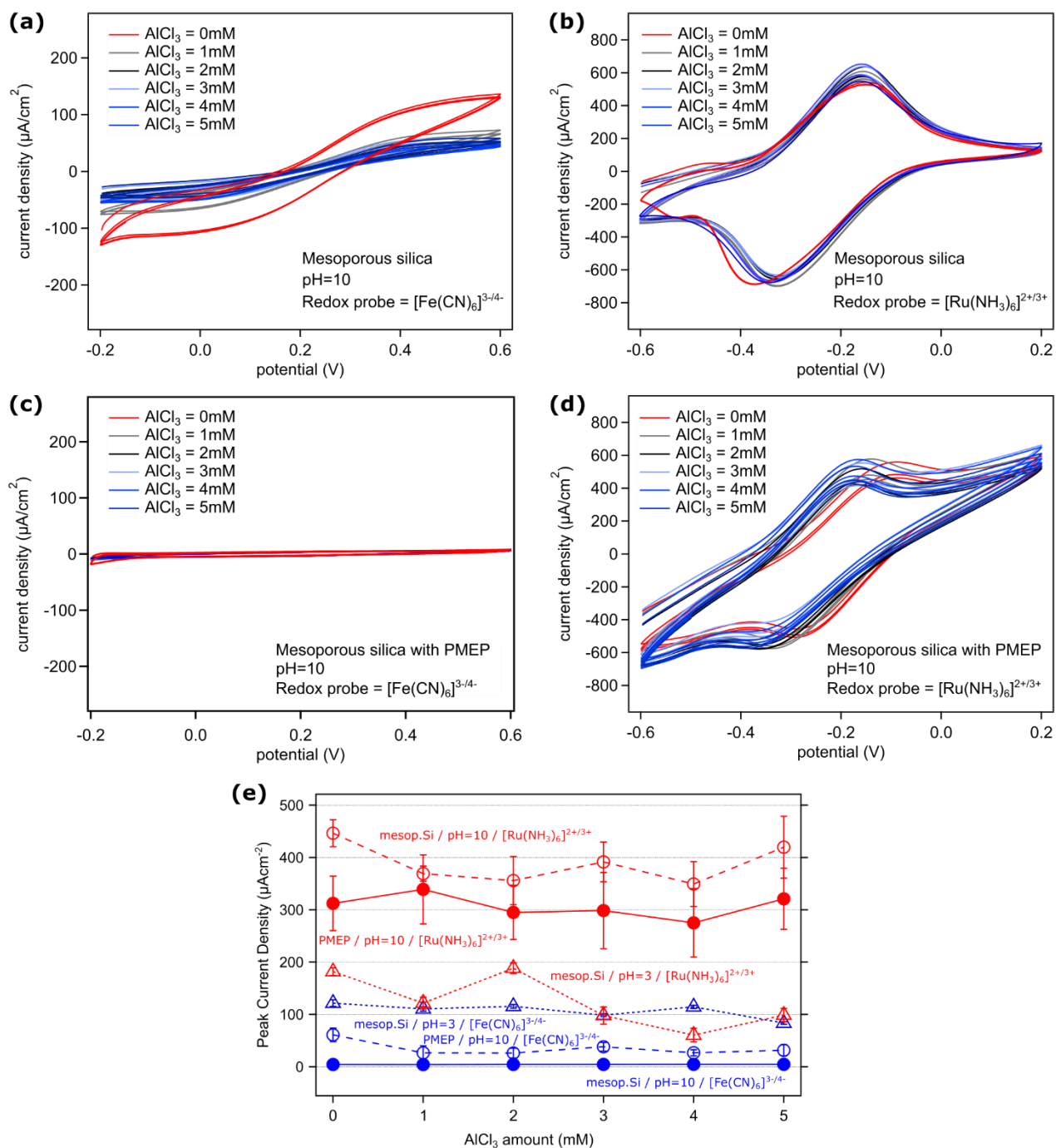


Figure S14. Cyclic voltammograms of mesoporous silica films (a-b) without and (c-d) with PMEP at their pores when the pores are in contact with electrolyte solutions with changing amounts of AlCl_3 inside. All the CV curves were collected at a pH=10 and by using (a,c) $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and (b,d) $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ as ionic probes. (e) Non-normalized peak current densities calculated from the CV curves in (a-d) and also CV curves collected from measurements using pH=3 electrolytes with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (blue triangles) or $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ (red triangles) as ionic probes. Error bars are sd.