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Insights into the Role of Counterions on Polyelectrolyte-modified Nanopore Accessibility

Laura Silies¹, Estefania Gonzalez Solveyra², Igal Szleifer^{*,2}, and Annette Andrieu-Brunsen^{1,*}

¹Ernst-Berl Institute für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 4, D-64287 Darmstadt, Germany

²Department of Biomedical Engineering, Department of Chemistry and Chemistry of Life Processes Institute, Northwestern University, Evanston, Illinois 60208, USA.

Abstract

Nanopores play a decisive role in different technologies from oil production, separation and sensing to drug delivery or catalysis and energy conversion. In recent years, abilities to functionalize nanopores have advanced significantly. Thereby nanopores functionalized with polyelectrolytes or responsive polymers show fascinating transport properties, such as gated or gradually controlled ionic permselectivity. Nonetheless, understanding the influence of external parameters such as ion type or concentration on nanopore performance, and thus on the mentioned applications, remains a challenge but is crucial for applications. In this work, the effect of different counterions on the wetting and ionic transport in poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PMETAC) functionalized silica mesopores (pore diameter < 10 nm) was experimentally and theoretically investigated. Static contact angles covered a range from 45 ° to almost 90° by exclusively changing the counterion. Ionic pore accessibility was also strongly dependent on the counterion present and was found to gradually change from accessible pores up to complete, pH-independent ion exclusion. Based on molecular theory calculations, these experimental observations were rationalized based on ion binding between the METAC monomers and the counterions. In addition, the theoretical framework provided a nanoscopic view into the molecular organization inside the pores, showing a strong dependence of ion concentration and ion distribution profiles along the pore radius in dependence of the present ions. The obtained insights on the role of counterion type and ion binding in nanopores are expected to have direct impact on the above-mentioned applications.

Graphical Abstract

*Corresponding author: brunsen@cellulose.tu-darmstadt.de / igalsz@northwestern.edu.

Supporting Information.

Additional material is provided with extensive characterization of the mesoporous film properties and ionic permselectivity. A full description of the molecular theory with the derivation of the equations and the molecular model employed are also presented, along with a discussion on the charge regulation of silanol groups and the local pH and polyelectrolyte organization within the PMETAC modified silica mesopores.

Keywords

mesoporous silica films; polyelectrolyte; counterion; wetting; ionic permselectivity; ion binding

INTRODUCTION

Nanopores play a decisive role in different fields from oil production, separation and sensing to drug delivery or catalysis and energy conversion. One challenge is to understand the influence of external parameters such as ion type or concentration on nanopore performance and thus on the mentioned applications. Another one is the design of smart nanopores with dynamically controllable transport properties. One typical strategy to tune nanopore performance, and thus to e.g. achieve dynamic control over pore accessibility and transport, is based on pore functionalization using responsive molecules or polymers. With this approach for example pH^{1–3}, ion⁴, light^{5–7}, redox^{8–9} responsive pores have been reported. In addition to the intended function using responsive functional groups or polymers, nanopore performance such as their accessibility or release can be extremely sensitive to changing environmental conditions such as solution composition. This is especially critical if the nanopores have to perform in real applications such as oil production, catalysis, energy conversion, separation and sensing while being in contact with solutions containing several molecular components.

The above-mentioned responsive control of pore characteristics such as ionic permselectivity or release is based on electrostatic interactions, pore wettability and ligand binding. In case of polyelectrolyte functionalized planar surfaces the presence of salt is known to induce dramatic changes in swelling degree and stiffness. The salt-induced collapse of polyelectrolyte brushes is mostly described as the result of a concentration dependent screening of the charges on the pendants groups.^{10–11} In addition to this electrostatic screening of charges, the presence of ions can result in specific interactions with the charged polymer brush.^{12–14} Recent theoretical studies concerning ion-pairing emphasize the importance of understanding ion-ion interactions at the molecular level and to differentiate between contact ion pairing and solvent mediated interactions.^{15–17} Regarding resulting surface properties it has been shown that wettability of charged organic planar films can be tuned by choosing the proper counterions.^{18–19}

Thus, the nature of counterions in the environment of polyelectrolyte brushes significantly influences their properties and resulting surface properties even on planar surfaces. Examples are lubrication and compressibility.²⁰ Several research groups as well demonstrated an effect of counterion nature on charged planar surfaces. For imidazolium monolayers on gold surfaces counterion dependent contact angles from 30° for Br⁻ to 50° for CF₃SO₃⁻ up to 65° for CF₃(SO₂)₂N⁻ were observed.²¹ Azzaroni and co-workers observed contact angle changes from 19° in the presence of phosphate up to 79° in the presence of perchlorate on poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PMETAC) brushes at planar substrates.²² Using PMETAC functionalized structured surfaces, such as cotton fabric, even superhydrophobicity was achieved by using fluorinated counterions and could be reproducibly switched to a hydrophilic state by changing the type of counterion to SCN⁻.²³

Despite these experimental and theoretical works on functionalized planar surfaces, the effect of counterion nature on polyelectrolyte modified mesopores is not yet systematically understood. While changing from planar to porous surfaces, wetting and polymer swelling should dramatically affect molecular mesopore accessibility and ionic permselectivity. Understanding counterion effects on wetting, ligand binding, and mesopore accessibility is expected to have immediate impact on mesopore applications such as (bio)separation, oil production, catalysis, and sensing but as well on the design of de-wetting surfaces in case fluorinated molecules are used.

Here, we experimentally investigate the wetting and ionic permselectivity of PMETAC functionalized mesoporous silica thin films (pore diameter < 10 nm) in the presence of different counterions. The experimental observations are further rationalized by a molecular theory proven to accurately describe this type of systems. This theoretical framework provided a detailed molecular organization of all the species (ions, solvent, and grafted polymers) inside the nanometer-sized pores and allowed us to systematically investigate the complex balances between the interactions in the system: steric repulsions, electrostatic interactions, and ion-ion specific interactions. We are able to tune ionic permselectivity from accessible pores to complete exclusion exclusively based on the nature of the counterion.

EXPERIMENTAL SECTION

Reagents.

[2-(Methacryloyloxy)ethyl]trimethylammonium chloride (METAC) solution 80% in water Pluronic[®] F127, N,N-Dimethylaminoethyl Methacrylate and 2-Ethylaminoethanol are purchased from Sigma-Aldrich. Tetraethoxysilane (TEOS), β-Propiolactone and sodium N,N-Diethyldithiocarbamate trihydrate are purchased from Alfa Aesar. p-(Chloromethyl)phenyltrimethoxysilane was purchased from abcr.

Synthesis of N,N-(Diethylamino)-dithiocarbonylbenzyl(trimethoxy)silane (SBDC).

SBDC is prepared according to a previous report.²⁴ Briefly, the sodium N,N-Diethyldithiocarbamate trihydrate is recrystallized in methanol before use. Sodium N,N-Diethyldithiocarbamate (1.46 g, 8.59 mmol) is dissolved in 10 ml dry THF and dropped to a

solution of p-(Chloromethyl)phenyltrimethoxysilane (1.89 ml, 8.59 mmol) in 10 ml dry THF. The solution is stirred for 3 h at room temperature and filtered afterwards. The THF is evaporated and the product is dried under vacuum to yield a yellow oil (yield 22%). The product is characterized by $^1\text{H-NMR}$. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.60 (d, $J = 8.1$ Hz, 2H, C_6H_4), 7.42 (d, $J = 8.1$ Hz, 2H, C_6H_4), 4.55 (s, 2H, CH_2S), 4.04 (q, $J = 6$ Hz, 2H, NCH_2), 3.73 (q, $J = 6$ Hz, 2H, NCH_2), 3.61 (s, 9H, $\text{Si}(\text{OCH}_3)_3$), 1.28 (t, $J = 7.2$ Hz, 6H, CH_3).

Mesoporous film preparation.²⁵

Mesoporous silica films are synthesized via a sol gel method based on the oxide precursor tetraethoxysilane (TEOS) in the presence of the template Pluronic[®] F127. The precursor solutions are stirred for 24 h and used to produce films by evaporation induced self-assembly (EISA)²⁶ on ITO-coated glass, glass, or silicon wafer substrates at 40–50% relative humidity and 298 K (2 mm/s withdrawing speed). The precursor solution is prepared using the following molar ratios: 1 TEOS: 0.0075 F127: 40 EtOH: 10 H_2O : 0.2 HCl. Freshly deposited films are stored at 50% relative humidity in a chamber for 1 h, followed by a stabilizing thermal treatment carried out in two successive 1 h steps at 60 and 130 °C. Consecutively, the temperature is increased by 1 °C per minute up to 350 °C. The mesopore template is removed at 350 °C for 2 h. Subsequently, the films are rinsed with ethanol and stored under ambient conditions until further use.

Surface grafting of SBDC.²⁷

The prepared mesoporous films are inserted in a 1 mM solution of SBDC in dry THF for 4 h at 70°C. Subsequently, the films are extracted in THF for 30 min.

Polymerization of [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (METAC).²⁷

SBDC-functionalized mesoporous silica films are degassed by several consecutive vacuum–nitrogen cycles and immersed into a degassed aqueous solution of METAC (50%) under a nitrogen atmosphere. To initiate polymerization, the samples are irradiated (Vilber Lourmat Bio-Link BLX cross-linker) at 365 nm ($P = 2 \text{ mW/cm}^2$). After polymerization, the films are extracted over night at room temperature in deionized water to remove non-covalently attached monomer.

Infrared spectroscopy measurements (IR).

IR is performed using a Spectrum One (Perkin Elmer) instrument in attenuated total reflection (ATR) mode. Mesoporous films are scratched from both sides of a glass substrate to record IR spectra in a range from 4000 to 600 cm^{-1} . The measured spectra are automatically background corrected and normalized to the Si-O-Si band at $\sim 1070 \text{ cm}^{-1}$. Out of two measurements an average absorption value including standard deviation is determined using the absorption of the C=O signal at 1728 cm^{-1} .

Ellipsometry.

Film thickness and refractive index are determined on silicon wafer substrates and measured using a Nanofilm EP3 imaging ellipsometer. One zone angle of incidence (AOI) variation

measurements are captured between AOIs of 40 and 80° with a 658 nm laser. The apparent film thickness and refractive indices are calculated from the measured angles Ψ and using the EP4 analysis software supplied with the instrument. The fitting parameters for the silicon oxide layer thickness on the wafer substrate ($d(\text{SiO}_x) = 2.8 \text{ nm}$) have been measured separately. The measured data is fitted with a one-layer box model. Multilayer models are increasing the uncertainty and did not yield better results. The fitting program is allowed to vary film thickness of the mesoporous silica thin films between 100–500 nm and the refractive index between 1.1–1.7. All films are measured at three marked positions before and after each functionalization step. Changes in film thickness and refractive index are calculated for each specific position. To determine the porosity from refractive indices the Bruggemann effective medium approximation was used as discussed elsewhere.^{25, 28}

Transmission Electron Microscopy (TEM).

TEM measurements were recorded using a FEI CM20 TEM microscope with a maximum resolution of 2.3 Å, equipped with a LAB-6 cathode and a CCD camera (Olympus), using an acceleration voltage of 200 kV. Samples are scratched from glass substrates and dispersed in some drops of ethanol. Subsequently, the suspension is placed onto a TEM grid.

Contact angle.

Contact angle measurements are performed using *Modell TBU90E Dataphysics instruments GmbH* with the Program *SCA-Software*. The mesoporous films modified with PMETAC are incubated with the corresponding counterion solution for 20 min and subsequently characterized regarding their dynamic contact angle measured using a 0.2 $\mu\text{l/s}$ rate with a final drop volume of 3 μl . The films are measured at different positions and the average value as well as the standard deviation is calculated. For the static contact angle a water volume of 3 μl is used.

Cyclic Voltammetry.

Quantitative variations in permselectivity are studied by following the changes of voltammetric peak currents associated with cationic $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ and anionic $\text{Fe}(\text{CN})_6^{4-/3-}$ redox species, diffusing across the mesoporous film are recorded with an Autolab PGSTAT302N (Metrohm). Mesoporous films modified with PMETAC are prepared on bare indium tin oxide (ITO) coated glass substrates which are used as working electrode. The measurements are performed with a 2 mM aqueous solution of the probe molecule in a 0.1 M or 0.01M solution of the different counterions as supporting electrolyte. The pH is adjusted with the corresponding acid of the different counterions. An Ag/AgCl electrode (BASi RE-6) serves as reference electrode, and various scan rates between 25 and 1000 mV.s^{-1} are measured. An electrode area of 0.21 cm^2 is measured.

Modeling of molecular organization inside mesopores.

The description of the molecular organization within the pore was calculated using a previously developed molecular theory (MT). The MT explicitly considers the size and shape of the molecular species, the charge distribution, the conformations and molecular volume of all molecules, the interactions among them (electrostatic and excluded volume),

and all coupled chemical equilibrium (acid-base, ion-binding, etc.)^{29–36}. The basic idea of the MT is to write the free energy of the system in terms of the probabilities of each different polymer conformation, the density profiles of solvent molecules and ions in the system, and the fraction of protonated/bound and deprotonated/unbound species. In a generic formulation of the theory, the free energy, F , is written as $F = -TS_{mix} - TS_{conf} + E_{rep} + E_{elec} + F_{chem}$ where T is the temperature, S_{mix} corresponds to the mixing (translational) entropy of the mobile species (i.e. water, anions, cations, etc.); S_{conf} is the conformational entropy of the polymers; E_{rep} contains the steric repulsive interactions between all the molecular species; E_{elec} is the total electrostatic energy and F_{chem} represents the free energy associated with the chemical equilibria present in the system (acid-base, ion binding, etc.). The exact expression of the free energy for different systems has to be derived *ad hoc*. Several examples have been reported in the literature.^{29, 33–34, 36–38}. The input for the MT is the set of conformations for the polymers and the values of the controlled variables (temperature, surface density, concentration of salt and redox probes, and pH). Minimization of the system's free energy yields the probability of each of polymer conformation, the spatial distribution of the mobile species, and the chemical state of all species, thus enabling the evaluation of structural and thermodynamic properties of the system at equilibrium. In this way, the MT allows the study of the complex couplings that occur between factors such as molecular organization, physical interactions, and changes in chemical state. Further details on the molecular model used in the calculations presented in this work can be found in the Supporting Information.

RESULTS AND DISCUSSION

To investigate the effect of different counterions on the wetting, ligand binding, and electrostatically controlled ionic permselectivity of polyelectrolyte functionalized mesopores, mesoporous thin silica films were modified with strong polyelectrolyte poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PMETAC) brushes using an iniferter-initiated polymerization.²⁷ It is known that counterion concentration and the nature of counterions affect the swelling state of polyelectrolyte brushes which can affect the wettability of planar surface.^{17, 39} The effect of selected counterions on the PMETAC swelling degree is determined by ellipsometry as summarized in Figure 1 for planar surfaces modified in analogy to the subsequently discussed mesoporous silica films. The gradual increase in swelling degree from $\text{ClO}_4^- < \text{Cl}^- < \text{PO}_4^{3-}$ is in accordance with literature reports.¹⁷

Mesoporous thin films have been prepared by dip coating resulting in a film thickness between 150–250 nm. The used mesoporous films templated with Pluronic® F127 are characterized by a porosity of 40–50 vol% as determined based on the refractive index extracted from ellipsometry measurements,²⁵ mesopore sizes of 6–7 nm and pore connections (necks) of ~3 nm. XPS measurements revealed one SBDC molecule per 3.3 silica atoms in the case of functionalization at an elevated temperature of 70 °C. Details on mesoporous film preparation and iniferter-initiated polymerization in pores can be found in an earlier report.²⁷ Based on this knowledge, ESI mass spectroscopy and infrared spectroscopy data (Figure 1b) we estimated an average polymer chain length of 2–5 monomers per chain within the mesopores as detected after de-grafting. The polymer on the

outer planar surface usually shows larger chain lengths (film thickness of up to 45 nm, Figure 1c). Based on the C=O stretching band of PMETAC at 1727cm^{-1} the polyelectrolyte amount is followed by infrared spectroscopy. All infrared spectra are normalized to the Si-O-Si stretching band at 1070cm^{-1} . Furthermore, the Si-OH stretching band at $\sim 966\text{cm}^{-1}$ is clearly visible. It is worth mentioning that the grafting density, or more precisely the iniferter density, is kept constant and equal to the value presented above, in all the experiments and calculations performed in this work. This was chosen such that the system was overall positively charged, and we could focus on the effect of counterions in the solution. It should be noted however, that modifying the grafting density, and hence the overall charge of the system, has a profound impact on the final behavior of the system. For a thorough discussion on this effect we refer the interested reader to reference²⁷.

Measuring dynamic contact angles at such a PMETAC modified mesoporous film surface after incubation into a counterion solution a strong variation of advancing macroscopic contact angle between 45° and almost 90° is observed (Figure 2a). The corresponding reference measurements without PMETAC modification are shown in Figure S8. Simultaneously, the receding macroscopic contact angle varies between 30° and 50° . Comparing the contact angle values to a study of Azzaroni et al. on planar surfaces the observed counterion influence (Figure 2a) is less dramatic. This might be due to a lower PMETAC amount (shorter chain length) and the mesoporous structure of the presented surfaces that takes up a part of the water droplet. A very interesting observation is the contact angle of almost 90° after introducing CF_3SO_3^- as counterion. The generally hydrophilic mesoporous surface becomes hydrophobic and shows a contact angle close to water exclusion. This indicates that a change from water exclusion to water penetration into the mesopores might be possible only by changing the counterion.

Besides a gradual adjustment of contact angle based on the nature of the counterion, a reversible change in advancing macroscopic contact angle in repeated cycles of counterion exchange is observed on PMETAC modified mesoporous films (Figure 2 b, c). A contact angle switching between approximately 50° and 70° is observed for changes between phosphate and perchlorate whereas reversible changes of the macroscopic advancing contact angle between approximately 50° and 75° are observed for changes between phosphate and CF_3SO_3^- . The difference in the absolute value of the measured contact angle most probably results from the solution composition of the droplet used. In Figure 2a a 0.1 M aqueous solution of the counterion was used to measure the macroscopic advancing and receding contact angles whereas distilled water was used for the measurements shown in Figure 2b,c. This difference in the absolute value of the obtained macroscopic advancing contact angle between Figure 2a and Figure 2b,c indicates the effect of counterion concentration which is further investigated in Figure 3e,f regarding ionic permselectivity.

The nature of the counterions was found to affect not only the wetting behavior of the pores, but also to strongly influence the ionic permselectivity (Figure 3). PMETAC modified mesoporous films are positively charged independently of the solution pH. Nevertheless, residual silanol groups might induce negative charges at the mesopore wall at basic pH (Figure S6). Comparing the measured ionic permselectivity at pH 3 and pH 9, no significant influence of residual silanol groups can be observed, indicating a PMETAC functionalization

along the entire mesoporous film. The positive charge of the mesopores and the presence of a defect free film is supported by the complete electrostatic exclusion of the positively charged probe molecule $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ independent of pH and type of counterion (Figure 3c,d). For the negatively charged probe molecule $[\text{Fe}(\text{CN})_6]^{3-/4-}$ the situation seems to be more complex. First the pH does not have a significant influence on the mesopore accessibility for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as well supporting a functionalization of the entire mesoporous film. But the nature of the counterion has a strong influence on the ionic permselectivity visible by a decreasing peak current from 7 μA for PO_4^{3-} and Cl^- which show a comparable ionic permselectivity, to 4 μA for ClO_4^- and complete $[\text{Fe}(\text{CN})_6]^{3-/4-}$ exclusion in the presence of CF_3SO_3^- . Treating the mesoporous films investigated in Figure 3 with CO_2 -plasma^{40–41} after iniferter binding to suppress PMETAC formation on the external mesoporous film surface the observed ionic permselectivity is comparable (Figure S1) and can be ascribed to PMETAC inside the spatial confinement of mesopores. Decreasing the counterion concentration by a factor of 10 to 0.01 M results in a decrease in I_p and a less pronounced difference in peak current for the different counterions (Figure 3e,f). This is most probably due to the decrease in conductivity of the solution because the counterion represents the supporting electrolyte. Consequently, the mesopore accessibility is suppressed in the presence of 0.1 M fluorinated CF_3SO_3^- and reduced in the presence of ClO_4^- as compared to the presence of PO_4^{3-} and Cl^- . The exclusion of any negatively charged probe molecule in the presence of CF_3SO_3^- might be associated to water exclusion due to the high contact angle of up to 90° (Figure 3a) or ligand binding. These results correspond to the increasing contact angle in the presence of ClO_4^- and CF_3SO_3^- but could not be explained based on PMETAC swelling and resulting “pore filling”.

Consequently, these experimental observations indicate a complex interplay of polyelectrolyte expansion, charge, wetting and ligand (counterion) binding on ionic mesopore accessibility and transport processes in mesopores as further on systematically investigated based on theoretical considerations.

Modeling of the molecular organization in silica mesopores modified

The experimental results discussed above show that there is an important effect of the counterion on the transport properties within the modified silica mesopores. To analyze this effect, theoretical calculations have been performed to determine the molecular organization for PMETAC functionalized mesopores containing either chloride (Cl^-) or triflic anion (CF_3SO_3^-) as the counterion. The molecular theory has been used recently to study similar systems (where only molecular volume and electrostatic interactions were considered),⁴² but it has been modified in this work to allow for the possibility of counterion-METAC ion binding. Several articles in the literature describe the tetraalkylammonium (moiety that is present in every METAC segment) as a hydrophobic cation.^{43–45} Similarly, the triflic anion has the hydrophobic moiety (CF_3). Liu and coworkers studied ion specific interactions between PMETAC polyelectrolytes and Hofmeister anions, and found that ion pairing can be observed for chaotropic anions (more hydrophobic) and that it is driven by both hydrophobic and electrostatic interactions.⁴⁶ Based on the hydrophobic nature of portions of both METAC segments and triflic anion, the possibility of ion binding was incorporated to the molecular theory framework previously developed.⁴² This is done by adding a term to the

free energy of the system corresponding to the ion-binding chemical equilibrium. It is worth noting that the hydrophobic effects are not considered separately in our calculations, but are instead included in the ion-binding term. The considered ion pairing between the triflic anion and the METAC segment is the following:

characterized by the corresponding binding constant: $K_{\text{ion bind}} = a_{\text{METAC-CF}_3\text{SO}_3} / (a_{\text{METAC}} + a_{\text{CF}_3\text{SO}_3^-})$ where $a_{\text{METAC-CF}_3\text{SO}_3}$, a_{METAC} , $a_{\text{CF}_3\text{SO}_3^-}$ correspond to the activities of the ion pair, the METAC monomers and the triflic anion respectively. Since the binding constant is not available in the literature, it is varied in a systematic manner to study its effect on the PMETAC functionalized mesopore characteristic. For both counterions studied, two scenarios are considered: the exclusive presence of molecular volume and electrostatics effects and the presence of additional ion-binding effects.

In our calculations, the mesopores were modeled as cylinders of 7 nm in diameter. The walls of the pores contain silanol groups and SBDC molecules to which PMETAC chains were grafted on. Following previous procedures,⁴² two types of silanol groups with different acid-base properties were considered (silanols Q2 and Q3 with pKa values of 8.2 and 2.0 respectively). Surface density of SBDC molecules, silanol groups, and polyelectrolyte molecules are taken as the values obtained experimentally from XPS, BET and TGA analysis, i.e., $\sigma_{\text{SiOH,Q3}} = 0.132 \text{ nm}^{-2}$, $\sigma_{\text{SiOH,Q2}} = 0.528 \text{ nm}^{-2}$, $\sigma_{\text{SBDC}} = \sigma_{\text{PMETAC}} = 0.2 \text{ nm}^{-2}$ (each SBDC group was assumed to have a PMETAC chain). The degree of polymerization is varied between 2 and 5 monomers per chain, as determined experimentally.

The hypothesis that the experimentally observed differences in transport are driven purely by an interplay between electrostatic interactions and the molecular volume differences of the counterions (i.e., no ion binding) was firstly analyzed. However, as can be seen in Figure 4, this scenario would lead to very similar in pore concentrations of the redox probes for both Cl^- and CF_3SO_3^- , at a given pH value and degree of polymerization. It can be observed that $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ is excluded from the pores for polyelectrolyte chains with more than 3 monomers and for all bulk pH values studied, whereas the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe increases its amount along the degree of polymerization. This is due to the electrostatic interactions between the probes and the positively charged PMETAC-modified nanopore. Only a small increase of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ and an exclusion of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ inside the pores are observed when they are grafted with very short polyelectrolyte molecules ($n_{\text{seg}} = 2$) and a basic pH. In this case, the high pH would favor the deprotonation of silanol groups on the pore walls, which would counterbalance the positive charges of the polyelectrolyte chains grafted to them. This lowers the electrostatic repulsions with the positively charged $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ probe molecule (enabling its entrance to the pore), while increasing the repulsions between the negatively charged $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe and the deprotonated silanol groups (excluding its molecules from the pore). For pores modified with polyelectrolyte chains of more than 3 monomers, this balance is not observed, and the net charge of the nanopore is positive. However, the increase of negative charges at the pore wall for pH= 9.0 (see Figure S6) decreases the overall positive charge inside the pores, and this explains the

lower in pore concentrations of the FC probe at this pH (Figure 4, right panel), as compared to pH=3.0 (Figure 4, left panel). (For a more comprehensive discussion on the interplay between the positively charged polyelectrolyte and the charge regulation of the silanol groups at the nanopore walls we refer the interested reader to Ref.⁴²)

MT calculations considering only ion volume and electrostatic effects allow explaining the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ exclusion from PMETAC modified mesopores in presence of CF_3SO_3^- under all investigated conditions (degree of polymerization and bulk solution pH), which corresponds to experimental results (Figure 3). However, it does not account for the exclusion of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ when CF_3SO_3^- is the counterion.

Consequently, further MT calculations allowing for ion binding between the CF_3SO_3^- counterion and the METAC monomers were performed. This would result in neutral ion-pairs. Since the value of the equilibrium constant for this ion pair formation has not been reported in the literature, it was systematically varied between 10^{-2} M^{-1} (no ion binding) to 10^{15} M^{-1} (corresponding to the biotin-streptavidin binding, one of the strongest binding constants known)⁴⁷⁻⁴⁸. The resulting $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ probe concentrations inside the PMETAC modified silica mesopores are shown in Figure 5 (note the different scale for each panel). At a first glance, the bulk solution's pH does not play a qualitative role independently of the probe molecule charge, in accordance to experimental results. We also observe that increasing the polyelectrolyte chain length increases the amount of positive charge anchored to the pore wall, increasing the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in pore concentration while decreasing the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$. Now, increasing the strength of the ion binding between CF_3SO_3^- - METAC monomers results in the gradual "neutralization" of the positively charged grafted polyelectrolytes inside the pores (since the ion pair is neutral), making the charge regulation of surface silanol groups a dominant factor. This implies going from positively charged pores when no ion binding is present, to negatively charged pores (from the deprotonation of surface silanol groups) when binding is very strong. This derives in opposite effects for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ probe molecule, given their opposite charges, as can be seen comparing upper and lower panels of Figure 5. Moreover, it can be observed that to achieve $[\text{Fe}(\text{CN})_6]^{3-/4-}$ exclusion in the presence of CF_3SO_3^- , a binding constant of 10^4 M^{-1} is needed. This would imply a binding constant for CF_3SO_3^- - PMETAC of at least 10^4 M^{-1} to account for experimental results for both probes. The value seems reasonable, considering that binding constants up to values in the range of 10^{13} - 10^{15} M^{-1} (biotin-streptavidin)⁴⁷ are known.

The nanoscopic detail provided by the MT also allowed to gain further insights into the molecular organization of the polyelectrolyte and ions along the pore diameter. Figure 6 compares the local concentration of METAC monomers, CF_3SO_3^- or Cl^- anions and probe molecules as a function of the distance from pore axis, for solutions containing Cl^- ions, in which no ion binding is considered, and CF_3SO_3^- ions, in which ion pairing with METAC monomers is included, with a K_{bind} of 10^{-4} M^{-1} . It can be observed that the distribution of the monomers shows a box-like behavior at a solution pH of 3 and a continuous decrease of polyelectrolyte volume fraction towards the pore center at a solution pH of 9, for both probe molecules. This is because increasing bulk solution pH leads to a more negatively charged surface (Figure S6). It is worth noting that the pH inside the mesopores is always higher as

compared to the pH in bulk solution, and it exhibits a profile along the pore radius that correlates with that of the polyelectrolyte layer (Figure S7). As can be seen from the counterions' profiles, the concentration of both CF_3SO_3^- or Cl^- anions is greater than the bulk concentration of 0.1 M, given the positively charged monomers grafted to the pore walls. Another feature shared by counterions in both systems (with and without ion binding) is their decrease in the proximity of the pore wall, more accentuated at bulk pH 9, driven by the negatively charged surface (Figure S6). However, binding vs. no binding has a significant effect in the profiles of CF_3SO_3^- vs. Cl^- along the pore. For the Cl^- counterions (no binding), its distribution along the pore is rather uniform, and there is an important amount of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe in the pore (much greater than the bulk concentration of 0.002 M). On the other hand, for the CF_3SO_3^- counterions (ion binding with K_{bind} of 10^{-4} M^{-1}), we observe a strong co-localization with the METAC monomers, corresponding to the formation of neutral ion pairs, and no significant amount of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe in the pore at both pH values studied. In the center of the pore, the concentration of free counterions is much higher than in bulk (0.1M), but given the partial neutralization of the positive METAC monomers, there is a smaller driving force for them to enter the pore. Hence the difference in concentration of free counterions for systems containing CF_3SO_3^- vs. Cl^- .

Our calculations suggest that ion binding between the anion CF_3SO_3^- and the METAC monomers explains the experimentally observed exclusion of both $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ probes, irrespective of bulk solution pH. Moreover, resorting to theoretical modeling allowed us to further study the behavior of the system on a molecular level, complementing experimental observations. The performed calculations reflect that redox probes exclusion or inclusion from the pores depends upon a rather complex balance of competing forces: excluded volume and electrostatics interactions, and chemical reactions (both acid-base of silanol groups and ion binding between the METAC monomers and the triflic anion).

Finally, even though the calculations presented above have been performed for Cl^- and CF_3SO_3^- anions, the insights gained from including ion binding between the counterion and the METAC monomers into our molecular model allow to be easily expanded to different counterions such as (Cl^- , PO_4^{3-} , ClO_4^- , CF_3SO_3^-). Following previous reports in the literature,⁴⁶ we incorporated the possibility of ion binding as the result of combined hydrophobic and electrostatic interactions between ions of different hydrophobicity. In a recent publication, Azzaroni *et al.* showed that the hydrophobic character follow the trend $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{PO}_4^{3-}$ with contact angles ranging from 79° to 19° .¹⁷ In our theoretical formulation, weaker hydrophobic interactions between the counterion and the METAC monomers (arising from the less hydrophobic character of the anion) would result in smaller K_{bind} values. Then, the resulting trends would follow those discussed above, since ion volume showed no significant effect. Namely, smaller K_{bind} values would result in only partial exclusion of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probes from the PMETAC modified silica mesopores, while completely excluding the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ probes, irrespective of bulk solution's pH (Figure 5 with $K_{\text{bind}} < 10^{-4} \text{ M}^{-1}$). These theoretical predictions would be in line with the obtained results, as reflected in Figure 3a–d.

CONCLUSIONS

In summary, this study experimentally shows and theoretically explains the modulation of mesopore accessibility for PMETAC functionalized mesopores in the presence of different counterions based on solution pH, PMETAC segment density and ion-polyelectrolyte binding constant for positively and negatively charged probe molecules. Essentially, PMETAC functionalized mesopores are not accessible for positively charged probe molecules due to the pH-independent electrostatic repulsion. The pore accessibility of negatively charged $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe molecules is strongly affected by the nature of the counterion. In solutions containing ClO_4^- , the accessibility is reduced as compared to the solutions of Cl^- and PO_4^{3-} . In the presence of CF_3SO_3^- no mesopore accessibility for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ is observed. This behavior is in agreement with an increasing contact angle in the presence of ClO_4^- and CF_3SO_3^- . These experimental observations are supported by MT calculations. Additionally, theory reveals a binding constant in between PMETAC and CF_3SO_3^- of $\sim 10^4$ and gives insights into the PMETAC and CF_3SO_3^- ion distribution along the mesopore radius. The pH inside the mesopores is determined to be always higher than the solution pH and the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe molecule exclusion depends on the ion-polyelectrolyte binding constant which we attribute to a complex balance between steric repulsion, electrostatic interactions and ion binding between the METAC monomers and the triflic anion. Based on this interplay, the presented results should be transferable to other polyelectrolyte functionalized porous systems which is expected to allow the rational design of porous materials for separation and sensing, ligand binding and release applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

1. Calvo A; Yameen B; Williams FJ; Soler-Illia GJAA; Azzaroni O, Mesoporous Films and Polymer Brushes Helping Each Other To Modulate Ionic Transport in Nanoconfined Environments. An Interesting Example of Synergism in Functional Hybrid Assemblies. *J. Am. Chem. Soc* 2009, 131, 10866–10868. [PubMed: 19722668]
2. Yameen B; Ali M; Neumann R; Ensinger W; Knoll W; Azzaroni O, Synthetic Proton-Gated Ion Channels via Single Solid-State Nanochannels Modified with Responsive Polymer Brushes. *Nano Lett.* 2009, 9, 2788–2793. [PubMed: 19518086]
3. Tagliazucchi M; Azzaroni O; Szleifer I, Responsive Polymers End-Tethered in Solid-State Nanochannels: When Nanoconfinement Really Matters. *J. Am. Chem. Soc* 2010, 132, 12404–12411. [PubMed: 20718436]
4. Brunsen A; Diaz C; Pietrasanta LI; Yameen B; Ceolin M; Soler-Illia GJAA; Azzaroni O, Proton and Calcium-Gated Ionic Mesochannels: Phosphate-Bearing Polymer Brushes Hosted in Mesoporous

Thin Films As Biomimetic Interfacial Architectures. *Langmuir* 2012, 28, 3583–3592. [PubMed: 22309103]

5. Brunsen A; Cui J; Ceolín M; Campo A; Soler-Illia GJJA; Azzaroni O, Light-activated gating and permselectivity in interfacial architectures combining “caged” polymer brushes and mesoporous thin films. *Chem. Commun* 2012, 48, 1422–1424.
6. Zhang M; Hou X; Wang J; Tian Y; Fan X; Zhai J; Jiang L, Light and pH Cooperative Nanofluidic Diode Using a Spiropyran-Functionalized Single Nanochannel. *Adv. Mater* 2012, 24 2424–2428. [PubMed: 22488964]
7. He D; He X; Wang K; Cao J; Zhao Y, A Photon-Fueled Gate-Like Delivery System Using i-Motif DNA Functionalized Mesoporous Silica Nanoparticles. *Adv. Funct. Mater* 2012, 22, 4704–4710.
8. Elbert J; Krohm F; Rüttiger C; Kienle S; Didzoleit H; Balzer BN; Hugel T; Stühn B; Gallei M; Brunsen A, Polymer-Modified Mesoporous Silica Thin Films for Redox-Mediated Selective Membrane Gating. *Adv. Funct. Mater* 2014, 24, 1591–1601.
9. Pérez-Mitta G; Marmisollé WA; Trautmann C; Toimil-Molares ME; Azzaroni O, Nanofluidic Diodes with Dynamic Rectification Properties Stemming from Reversible Electrochemical Conversions in Conducting Polymers. *J. Am. Chem. Soc* 2015, 137, 15382–15385. [PubMed: 26587977]
10. Rühle J; Ballauff M; Biesalski M; Dziezok P; Gröhn F; Johannsmann D; Houbenov N; Hugenberg N; Konradi R; Minko S; Motornov M; Netz R; Schmidt M; Seidel C; Stamm M; Stephan T; Usov D; Zhang H, Polyelectrolyte Brushes In Polyelectrolytes with Defined Molecular Architecture I, Schmidt M, Ed. Springer Berlin Heidelberg: 2004; Vol. 165, pp 79–150.
11. Balazs AC; Singh C; Zhulina E; Chern S-S; Lyatskaya Y; Pickett G, Theory of polymer chains tethered at interfaces. *Progress in Surface Science* 1997, 55, 181–269.
12. Volk N; Vollmer D; Schmidt M; Oppermann W; Huber K, Conformation and Phase Diagrams of Flexible Polyelectrolytes In Polyelectrolytes with Defined Molecular Architecture II, Schmidt M, Ed. Springer Berlin Heidelberg: 2004; Vol. 166, pp 29–65.
13. Mei Y; Ballauff M, Effect of counterions on the swelling of spherical polyelectrolyte brushes. *Eur. Phys. J. E* 2005, 16, 341–349. [PubMed: 15685435]
14. Konradi R; Rühle J, Interaction of Poly(methacrylic acid) Brushes with Metal Ions: Swelling Properties. *Macromolecules* 2005, 38, 4345–4354.
15. Ganguly P; Schravendijk P; Hess B; van der Vegt NFA, Ion Pairing in Aqueous Electrolyte Solutions with Biologically Relevant Anions. *The Journal of Physical Chemistry B* 2011, 115, 3734–3739. [PubMed: 21410261]
16. Riccardi E; Wang J-C; Liapis AI, Molecular Modeling of Polymeric Adsorbent Media: The Effects of Counter-ions on Ligand Immobilization and Pore Structure. *J. Sep. Sci* 2012, 35, 3073. [PubMed: 23086680]
17. Azzaroni O; Brown AA; Huck WTS, Tunable Wettability by Clicking Counterions Into Polyelectrolyte Brushes. *Adv. Mater* 2007, 19, 151–154.
18. Shen Y; Zhang Y; Zhang Q; Niu L; You T; Ivaska A, Immobilization of ionic liquid with polyelectrolyte as carrier. *Chem. Commun* 2005, 4193–4195.
19. Lee BS; Chi YS; Lee JK; Choi IS; Song CE; Namgoong SK; Lee SG, Imidazolium ion-terminated self-assembled monolayers on Au: effects of counteranions on surface wettability. *J. Am. Chem. Soc* 2004, 126, 480–481. [PubMed: 14719941]
20. Raviv U; Giasson S; Kampf N; Gohy J-F; Jerome R; Klein J, Lubrication by charged polymers. *Nature* 2003, 425, 163–165. [PubMed: 12968175]
21. Lee BS; Chi YS; Lee JK; Choi IS; Song CE; Namgoong SK; Lee S. g., Imidazolium Ion-Terminated Self-Assembled Monolayers on Au: Effects of Counteranions on Surface Wettability. *Journal of the American Chemical Society* 2004, 126, 480–481. [PubMed: 14719941]
22. Azzaroni O; Brown AA; Huck WTS, Tunable Wettability by Clicking Counterions Into Polyelectrolyte Brushes. *Advanced materials* 2007, 19, 151–154.
23. Jiang C; Wang Q; Wang T, Tunable wettability via counterion exchange of polyelectrolyte brushes grafted on cotton fabric. *New. J. Chem* 2012, 36, 1641–1645.

24. de Boer B; Simon HK; Werts PL; van der Vegte EW; Hadzioannou G, "Living" Free Radical Photopolymerization Initiated from Surface-Grafted Iniferter Monolayers. *Macromolecules* 2000, 33, 349–356.
25. Boissiere C; Grosso D; Lepoutre S; Nicole L; Bruneau AB; Sanchez C, Porosity and mechanical properties of mesoporous thin films assessed by environmental ellipsometric porosimetry. *Langmuir* 2005, 21, 12362–12371. [PubMed: 16343015]
26. Brinker CJ; Lu Y; Sellinger A; Fan H, Evaporation-Induced Self-Assembly: Nanostructures Made Easy. *Adv. Mater* 1999, 11, 579–585.
27. Silies L; Didzoleit H; Hess C; Stühn B; Andrieu-Brunsen A, Mesoporous Thin Films, Zwitterionic Monomers, and Iniferter-Initiated Polymerization: Polymerization in a Confined Space. *Chem. Mater* 2015, 27, 1971–1981.
28. Brunsen A; Calvo A; Williams FJ; Soler-Illia GJAA; Azzaroni O, Manipulation of Molecular Transport into Mesoporous Silica Thin Films by the Infiltration of Polyelectrolytes. *Langmuir* 2011, 27, 4328–4333. [PubMed: 21425821]
29. Tagliazucchi M; Szleifer I, How does confinement change ligand–receptor binding equilibrium? Protein binding in nanopores and nanochannels. *J. Am. Chem. Soc* 2015, 137, 12539–12551. [PubMed: 26368839]
30. Narambuena CF; Longo GS; Szleifer I, Lysozyme adsorption in pH-responsive hydrogel thin-films: the non-trivial role of acid & base equilibrium. *Soft Matter* 2015, 11, 6669–6679. [PubMed: 26219383]
31. Ren C; Carvajal D; Shull KR; Szleifer I, Streptavidin–biotin binding in the presence of a polymer spacer. A theoretical description. *Langmuir* 2009, 25, 12283–12292. [PubMed: 19821628]
32. Longo GS; Thompson DH; Szleifer I, Ligand–receptor interactions between surfaces: the role of binary polymer spacers. *Langmuir* 2008, 24, 10324–10333. [PubMed: 18698869]
33. Nap RJ; Gong P; Szleifer I, Weak polyelectrolytes tethered to surfaces: effect of geometry, acid–base equilibrium and electrical permittivity. *J. Polym. Sci. B Polym. Phys* 2006, 44, 2638–2662.
34. Longo GS; Szleifer I, Ligand–receptor interactions in tethered polymer layers. *Langmuir* 2005, 21, 11342–11351. [PubMed: 16285809]
35. Fang F; Szleifer I, Kinetics and thermodynamics of protein adsorption: a generalized molecular theoretical approach. *Biophysical Journal* 2001, 80, 2568–2589. [PubMed: 11371435]
36. Szleifer I, Protein adsorption on surfaces with grafted polymers: a theoretical approach. *Biophysical Journal* 1997, 72, 595–612. [PubMed: 9017189]
37. Nap RJ; Szleifer I, How to optimize binding of coated nanoparticles: coupling of physical interactions, molecular organization and chemical state. *Biomater. Sci* 2013, 1, 814. [PubMed: 23930222]
38. Fang; Szleifer I, Effect of molecular structure on the adsorption of protein on surfaces with grafted polymers. *Langmuir* 2002, 18, 5497–5510.
39. Biesalski M; Johannsmann D; Rühle J, Electrolyte-induced collapse of a polyelectrolyte brush. *J. Chem. Phys* 2004, 120, 8807–8814. [PubMed: 15267812]
40. Babu DJ; Yadav S; Heinlein T; Cherkashinin G; Schneider JJ, Carbon Dioxide Plasma as a Versatile Medium for Purification and Functionalization of Vertically Aligned Carbon Nanotubes. *J. Phys. Chem. C* 2014, 118, 12028–12034.
41. Krohm F; Didzoleit H; Schulze M; Dietz C; Stark RW; Hess C; Stühn B; Brunsen A, Controlling Polymerization Initiator Concentration in Mesoporous Silica Thin Films. *Langmuir* 2014, 30, 369–379. [PubMed: 24364647]
42. Andrieu-Brunsen A; Micoureaux S; Tagliazucchi M; Szleifer I; Azzaroni O; Soler-Illia G. J. d. A., Mesoporous Hybrid Thin Film Membranes with PMETAC@Silica Architectures: Controlling Ionic Gating through the Tuning of Polyelectrolyte Density. *Chem. Mater* 2015, 27, 808–821.
43. Bhowmik D; Malikova N; Mériguet G; Bernard O; Teixeira J; Turq P, Aqueous solutions of tetraalkylammonium halides: ion hydration, dynamics and ion–ion interactions in light of steric effects. *Phys. Chem. Chem. Phys* 2014, 16, 13447. [PubMed: 24887596]
44. Krienke H; Vlachy V; Ahn-Ercan G; Bakó I, Modeling Tetraalkylammonium Halide Salts in Water: How Hydrophobic and Electrostatic Interactions Shape the Thermodynamic Properties. *J Phys Chem B* 2009, 113, 4360–4371. [PubMed: 19253971]

45. Marcus Y, Tetraalkylammonium Ions in Aqueous and Non-aqueous Solutions. *Journal of Solution Chemistry* 2008, 37, 1071–1098.
46. Kou R; Zhang J; Wang T; Liu G, Interactions between Polyelectrolyte Brushes and Hofmeister Ions: Chaotropes versus Kosmotropes. *Langmuir* 2015, 31, 10461–10468. [PubMed: 26359677]
47. Merkel R; Nassoy P; Leung A; Ritchie K; Evans E, Energy landscapes of receptor-ligand bonds explored with dynamic force spectroscopy. *Nature* 1999, 397, 50–53. [PubMed: 9892352]
48. Weber PC; Ohlendorf DH; Wendoloski JJ; Salemme FR, Structural origins of high-affinity biotin binding to streptavidin. *Science* 1989, 243, 85. [PubMed: 2911722]

Figure 1.

a) TEM image of a mesoporous silica film and **b)** infrared spectroscopy image of a PMETAC modified mesoporous silica film (red) in comparison to an untreated mesoporous silica film (black). **c)** Effect of different counterions on the swelling degree of PMETAC brushes at a planar silicon wafer surface as determined by ellipsometry. The silicon wafer was functionalized in analogy to the mesoporous silica films and serves as a reference for the PMETAC behavior on the external planar mesoporous film surface. The obtained results are schematically summarized in the table.

Figure 2.

a) Advancing and receding macroscopic contact angles in dependence of the counterion measured using an aqueous counterion solution with a concentration of 0.1M. **b)** Reversible switching of advancing contact angle between PO_4^{3-} and ClO_4^- and c) between PO_4^{3-} and CF_3SO_3^- measured using distilled water droplets after incubation into a counterion solution with a concentration of 0.1 M.

Figure 3.

Ionic permselectivity detected based on cyclic voltammetry using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at pH 3 (a) and pH 9 (b) and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ at pH 3 (c) and pH 9 (d) as probe molecules in the presence of different counterions at a counterion concentration of 0.1 M (a-e) and a counterion concentration of 0.01 M (f).

Figure 4: Averaged in pore concentration of the FC and RU probes as a function of the polyelectrolyte chain length, for both counterions (Cl^- and $CF_3SO_3^-$) without considering ion binding, for pH values of 3.0 (left panel) and 9.0 (right panel). Salt concentration = 0.1 M, redox probe concentration = $2 \cdot 10^{-3}$ M, $\sigma_{pol} = 0.2 \text{ nm}^{-2}$.

Figure 5: Averaged in pore concentration of the FC and RU probes (upper and lower rows respectively) as a function of the log of the binding constant for pH values of 3.0 (left panels) and 9.0 (right panels). Results correspond to CF_3SO_3^- anion solutions and pores modified with polyelectrolyte chains of different length (as indicated in the legend). Salt concentration = 0.1 M, redox probe concentration = $2 \cdot 10^{-3}$ M, $\sigma_{\text{pol}} = 0.2 \text{ nm}^{-2}$.

Figure 6:

Molar concentration of PMETAC monomers (full lines), total CF_3SO_3^- or Cl^- anions (dashed lines) and probe molecules (dotted lines) as a function of the distance from pore axis for both FC and RU probes (upper and lower rows respectively) and for triflic and Cl^- solutions (as indicated in the legend). $N_{\text{seg}} = 5$, salt concentration = 0.1 M, redox probe concentration = 2.10^{-3} M, $\sigma_{\text{pol}} = 0.2 \text{ nm}^{-2}$, pH values of 3.0 (left panels) and 9.0 (right panels).