

Supporting Information

Mixed Mosaic Membranes Prepared by Layer-by-Layer Assembly for Ionic Separations

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S1. Polyelectrolytes used in the preparation of polymeric nanotubes and mixed mosaic membranes (MMMs)

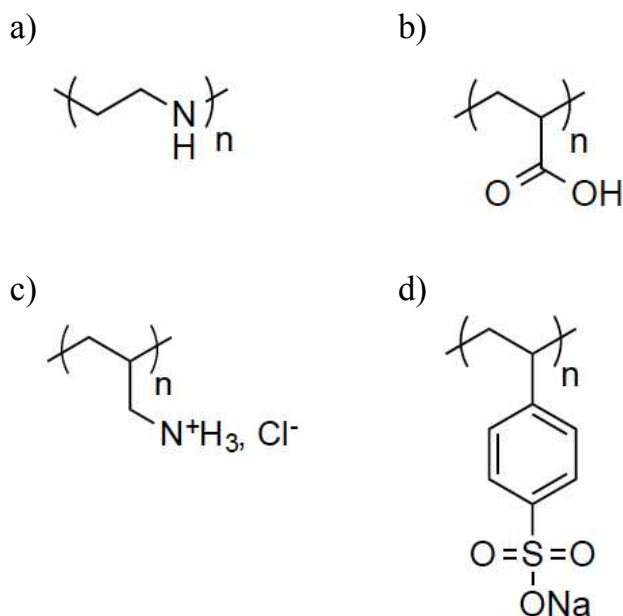


Figure S1. Chemical repeat units of the polyelectrolytes used in the present study. a) polyethylenimine (PEI); b) polyacrylic acid (PAA); c) polyallylamine hydrochloride (PAH) and (d) polystyrene sulfonate (PSS). Multilayer build ups of PAA and PAH were used to prepared the robust walls of the polymeric nanotubes. PEI and PSS were used to terminate the multilayer builds and produce polymeric nanotubes with cores lined by positively-charged and negatively-charged moieties, respectively.

S2. The effect of cation valency on the deposition of polyacrylic acid

The effect that the valence of the cation dissolved in the supporting electrolyte has on the thickness of the nanotube walls was studied by building the multilayers from solutions with supporting electrolytes containing a monovalent (NaCl) or divalent (CaCl_2) cation. Figure S2 shows SEM micrographs of the top surface of the PCTE templates from the different polyelectrolytes depositions solutions. As can be seen in the micrographs, the surface pores of the template were altered minimally when 0.5 M NaCl was used as the supporting electrolyte, but were completely filled when 35 mM CaCl_2 was implemented as the supporting electrolyte.

This can be rationalized by the conformation of polyacrylic acid in solution. In the presence of a monovalent cation, the polyacrylic acid molecules have an extended rod-like conformation, which makes it difficult for them to diffuse into the pores of the PCTE template.¹ However the divalent ions in solution associate with some of the repeat units along the backbone of the polyacrylic acid molecules, which reverses the charge of these repeat units. Electrostatic interactions cause the now positively-charged repeat units to interact with the negatively-charged repeat units (*i.e.*, repeat units that are not associated with a divalent cation). This bridging effect reduces the radius of gyration of the polyelectrolyte in solution, and facilitates access into the pores.² It is worth mentioning that, if the concentration of the divalent salt exceeds 35 mM the number of polyelectrolytes diffusing in to the pores is reduced considerably due to entropic barrier.²

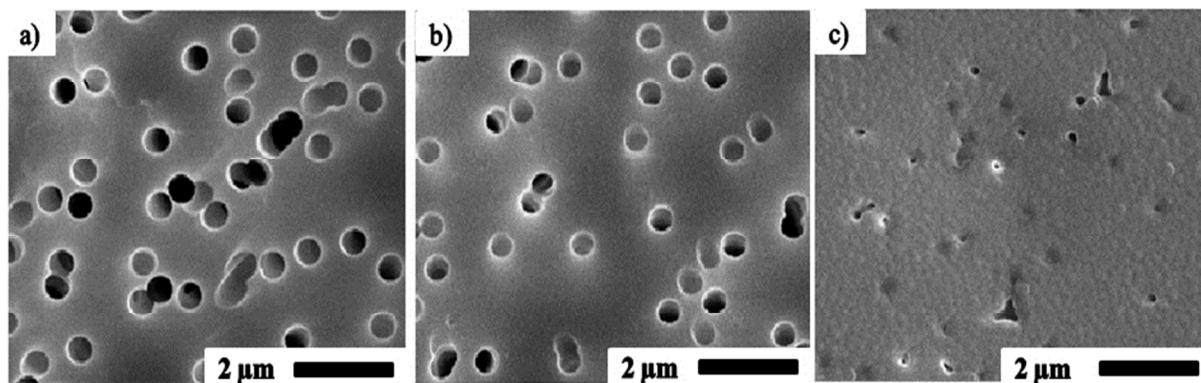


Figure S2. Scanning electron micrographs of (a) the polycarbonate track-etched (PCTE) membrane used as a template for the formation of polymeric nanotubes; (b) a PCTE template modified with 0.5 M NaCl as the supporting electrolyte; (c) a PCTE template modified using 35 mM CaCl_2 as the supporting electrolyte. Ten bilayers of PAA and PAH were used to modify the PCTE membranes.

S3. Influence of the pH and ionic strength of the LbL deposition solution on the nanostructure of the resulting polymeric nanotubes

As shown in Figure S3, the structure and thickness of the nanotube walls varied significantly with the composition of the solutions used for polyelectrolyte deposition. Fifteen bilayers of PAA and PAH were used to fabricate all of the nanotubes shown in Figure S3 (*i.e.*, the tube walls comprised [PEI (PAA/PAH)_{15.0}]). The nanotubes in Figure S3a were made from solutions containing 0.5 M NaCl and 35 mM CuCl₂ as the supporting electrolyte. The pH of the solutions were not adjusted after dissolving the polyelectrolytes, which produced solutions with a pH of 10.5, 2.5, and 4.0 for PEI, PAA, and PAH, respectively. As shown by the micrograph, these tubes were collapsed with rough walls. It was possible to produce more stable nanotubes by adjusting the pH of the deposition solution to 5.5 using HCl and NaOH as needed. The greater number of ionized repeat units at pH 5.5 leads to stronger interactions between the layers within the nanotube walls. However, the wall thickness of these nanotubes were in the range of 50 to 60 nm. Using these conditions, constructing enough bilayers to reduce the inner diameter of the nanotubes to ~20 nm would take an excessive length of time. Therefore, the preparation of nanotubes in the presence of CaCl₂ was explored. Nanotubes prepared from solutions containing CaCl₂ at the unadjusted pH of the dissolved polyelectrolytes had wall thickness in the range of 200 to 225 nm (Figure S3c). The nanotubes appear closed when depositing the polyelectrolytes from solutions adjusted to pH 5.5 (Figure S3d). From these results, it can be concluded that the thickness of the nanotubes walls prepared in presence of CaCl₂ were higher than those prepared using CuCl₂. The exact reason for this is not understood clearly but might be attributed to the strength of the interactions between the PAA repeat units and the divalent cation. Because solutions with a pH of 5.5 containing 0.5 M NaCl and 35 mM CaCl₂ as the supporting electrolyte

allowed us to build up the wall thickness of the polymer nanotubes more quickly we used this as the final formulation for the preparation of anionic and cationic tubes. It only took twelve bilayers to generate the desired nanostructure (Figure 1c) using this formulation. It was generally accepted that, thickness of the multilayer films prepared in a confined geometry is larger than that on flat surfaces due to the incomplete drainage of the polymer solution during LbL process,³ stronger polyelectrolyte deposition due to the curvature effect of pores⁴ and entanglement of polyelectrolyte in the confined geometry.⁵ Interestingly, these wall thicknesses values were much higher than that of the corresponding polymeric nanotubes prepared from similar substrates under same experimental conditions.⁴ We strongly believe this difference in thickness was due to adjusting the pH of the polyelectrolyte solutions used in during our LbL deposition process. At pH 5.5, most of the carboxylic acid moieties of the PAA are deprotonated and form complexes with the dissolved calcium ions. This in turn significantly affects the polymer chain conformation and aggregation state of the polymer.⁶ Therefore, in future efforts it could be possible to change the thickness of the pore walls by adjusting the solution pH of the polyelectrolyte solutions used during the LbL assembly.

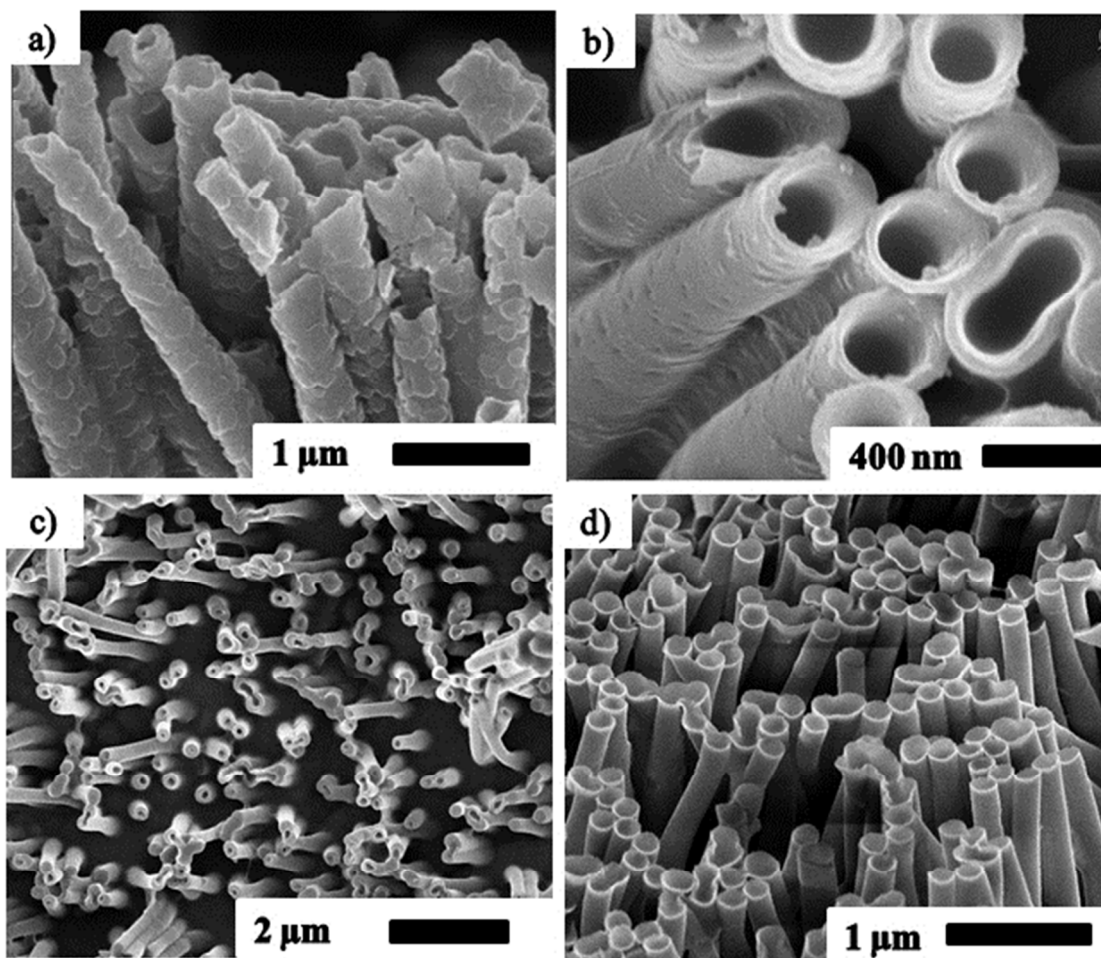


Figure S3. Polymeric nanotubes prepared using various experimental conditions. In panels (a) and (c) the pH of the deposition solutions were unaltered (*i.e.*, PEI: 10.5; PAA: 2.5; PAH: 4.0); in panels (b) and (d) the pH of the deposition solutions were adjusted to 5.5 using NaOH and HCl as needed. In panels (a) and (b) 0.5 M NaCl and 35 mM CuCl_2 was used as the supporting electrolytes; in panels (c) and (d) 0.5 M NaCl and 35 mM CaCl_2 was used as the supporting electrolytes.

S4. Preparation of mixed mosaic membranes

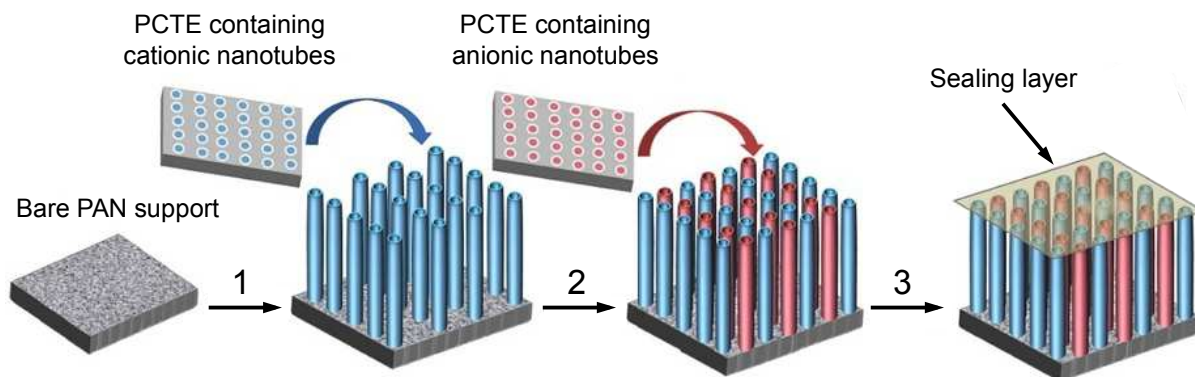


Figure S4. A schematic representation of the steps used to prepare mixed mosaic membranes (MMMs). A polyacrylonitrile (PAN) membrane, which has been soaked in a 1 M aqueous solution of sodium hydroxide at 55 °C for 1 h, is used as a substrate for the MMMs. (1) First, a polycarbonate track-etched (PCTE) membrane containing PEI-terminated nanotubes is placed gently on a damp PAN support. The water used to wet the PAN membrane helps the PCTE membrane to adhere evenly to the surface of the support. The PAN-PCTE composite is then heated in an oven at 80 °C for 1 h to facilitate the attachment of the cationic nanotubes to the surface of the PAN support. Subsequently, the PCTE template is removed selectively by immersing the whole composite in dichloromethane. These steps produce a membrane with vertically-aligned cationic nanotubes (blue cylinders) attached to the top surface of the PAN substrate. The nanostructure of the membrane at this stage of the fabrication process is displayed in Figure 4a of the main text. (2) The process (*i.e.*, attach PCTE membrane, heat treatment, and dissolution of the PCTE template) is then repeated using a PCTE membrane containing PSS-terminate nanotubes. The nanostructure of the membrane at this stage of the fabrication process is displayed in Figure 4b of the main text. (3) After the anionic nanotubes are deposited on the surface of the PAN substrate, a sealing layer is formed on the top of the multicomponent structure that possesses both anionic (red cylinders) and cationic (blue cylinders) domains that are accessible for transport. In this study, the sealing layer was formed using layer-by-layer assembly to deposit 3.5 bilayers of polyallylamine hydrochloride and polyacrylic acid. Cross sectional views of the nanostructure of the final MMMs are displayed in Figure 4c and Figure 4d of the main text.

S5. Photographs of the membrane throughout the nanotube adhesion process

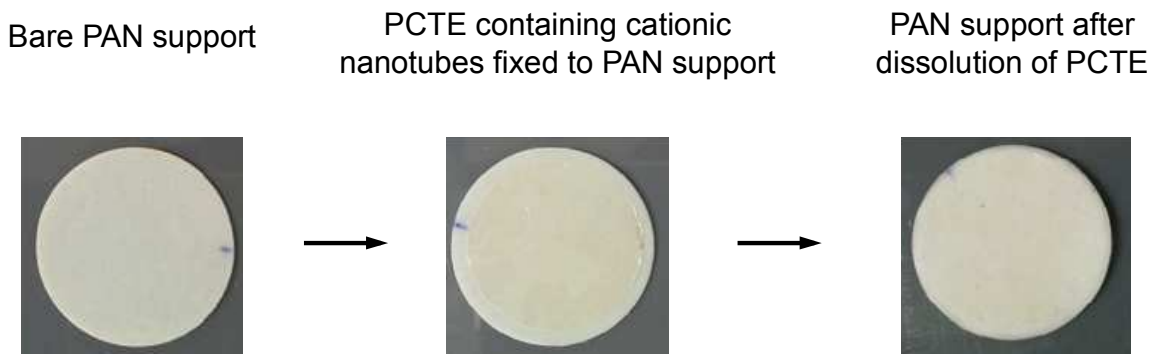


Figure S5. Photographs of the membrane throughout the process used to attach cationic nanotubes to the surface of the PAN substrate. To begin, a bare PAN membrane is immersed in a 1 M aqueous sodium hydroxide solution at 55 °C for 1 h. After rinsing the PAN substrate with DI water, a PCTE membrane containing positively-charged nanotubes is placed on top of it. As shown in the center panel, it is important to ensure that the PCTE membrane lies smoothly (*i.e.*, it should be wrinkle-free) on top of the PAN support prior to putting the PAN-PCTE composite into the oven. After 1 h in an oven at 80 °C, the composite is immersed in dichloromethane to selectively dissolve the PCTE membrane leaving cationic nanotubes attached to the surface of the PAN support. The image on the right shows the PAN support with vertically-aligned cationic nanotubes fixed to the surface (*i.e.*, the nanostructure of the membrane shown on the right is displayed in Figure 4a of the main text). Note that no PCTE membrane should be visible before beginning to attach the negatively-charged nanotubes onto the surface of the membrane. This may require multiple rinses with dichloromethane.

S6. Pure water flux of mixed mosaic membranes

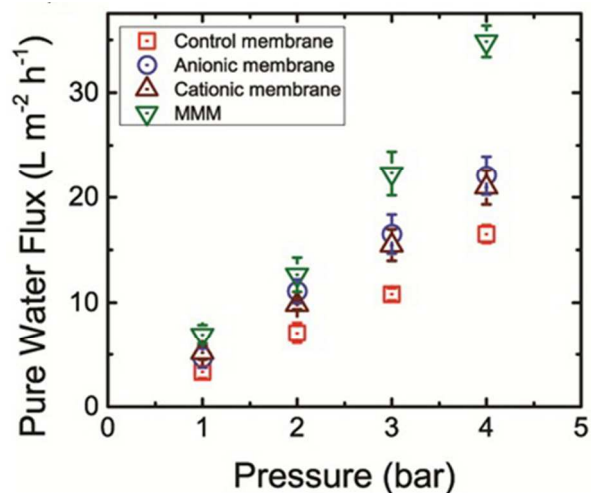


Figure S6. Comparison of pure water flux through four different membranes. The control membrane was made by depositing the sealing layer (*i.e.*, 3.5 bilayers of PAH and PAA) directly onto the PAN support membrane, anionic membranes were produced by functionalizing the PAN support with PSS-terminated nanotubes then applying the sealing layer, cationic membranes were produced by functionalizing the PAN support with PEI-terminated nanotubes then depositing the sealing layer, and the MMMs were produced by functionalizing the PAN support with both PEI-terminated and PSS-terminated nanotubes before applying the sealing layer. Error bar represents the standard deviation ($n=3$).

S7. Solute rejection data for mixed mosaic membranes challenged with mixed solute solutions

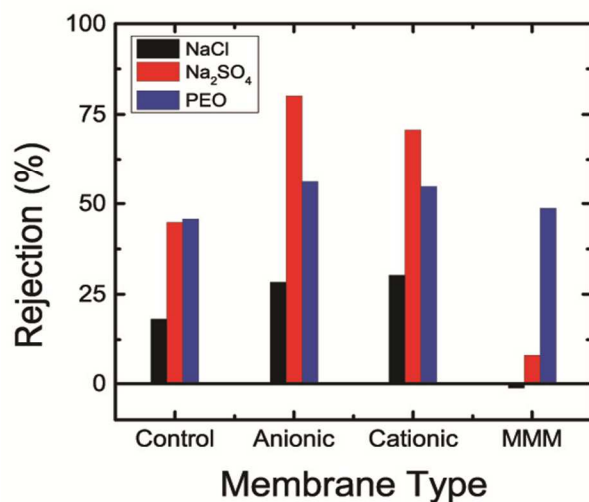


Figure S7. Rejection results of the mixed solutions of charged and neutral molecules. The control membrane was made by depositing the sealing layer (*i.e.*, 3.5 bilayers of PAH and PAA) directly onto the PAN support membrane, anionic membranes were produced by functionalizing the PAN support with PSS-terminated nanotubes then applying the sealing layer, cationic membranes were produced by functionalizing the PAN support with PEI-terminated nanotubes then depositing the sealing layer, and the MMMs were produced by functionalizing the PAN support with both PEI-terminated and PSS-terminated nanotubes before applying the sealing layer. Polyethylene oxide (PEO) with a molar mass of 2.0 kDa was used as the neutral solute (1g L⁻¹). Samples of the feed and permeate solutions were collected and the concentration of PEO was analyzed using total carbon analysis. Two different charged solutes Na₂SO₄ and NaCl were mixed with PEO. The salt was dissolved in the feed solution at a concentration of 10 mM. Samples of the feed and permeate solutions were collected and the salt concentrations were analyzed using ion chromatography. All experiments were carried out at an applied pressure of 4 bar.

S8. Solute rejection data for mixed mosaic membranes challenged with 0.1 mM salt solutions

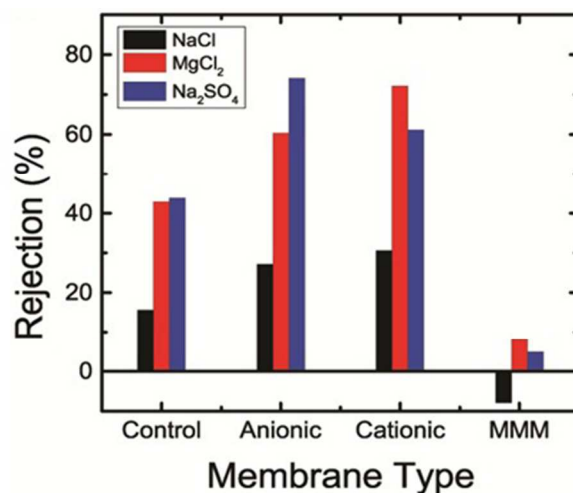


Figure S8. Comparison of solute rejection for charged solutes between four different membranes. The control membrane was made by depositing the sealing layer (*i.e.*, 3.5 bilayers of PAH and PAA) directly onto the PAN support membrane, anionic membranes were produced by functionalizing the PAN support with PSS-terminated nanotubes then applying the sealing layer, cationic membranes were produced by functionalizing the PAN support with PEI-terminated nanotubes then depositing the sealing layer, and the MMMs were produced by functionalizing the PAN support with both PEI-terminated and PSS-terminated nanotubes before applying the sealing layer. Three different charged solutes, MgCl₂, Na₂SO₄ and NaCl, were used. Samples of the feed and permeate solutions were collected and the salt concentrations were analyzed using a conductivity probe and ion chromatography. The salt was dissolved in the feed solution at a concentration of 0.1 mM. All experiments were carried out at an applied pressure of 4 bar.

References

1. Zhang, L.; Vidyasagar, A.; Lutkenhaus, J. Fabrication and Thermal Analysis of Layer-by-Layer Micro- and Nanotubes. *Curr. Opin. Colloid Interface Sci.* 2012, 17, 114-121.
2. Cho, Y.; Lee, W.; Jhon, Y.; Genzer, J.; Char, K. Polymer Nanotubules Obtained by Layer-by-Layer Deposition Within AAO-Membrane Templates with Sub-100-nm Pore Diameters. *Small* 2010, 6, 2683-2689.
3. Lee, D.; Cohen, R. E.; Rubner, M. F. Antibacterial Properties of Ag Nanoparticle Loaded Multilayers and Formation of Magnetically Directed Antibacterial Microparticles. *Langmuir* 2005, 21, 9651-9659.
4. Ai, S.; Lu, G.; He, Q.; Li, J. Highly Flexible Polyelectrolyte Nanotubes. *J. Am. Chem. Soc.* 2003, 125, 11140-11141.
5. Alem, H.; Blondeau, F.; Glinel, K.; Demoustier-Champagne, S.; Jonas, A. M. Layer-by-Layer Assembly of Polyelectrolytes in Nanopores. *Macromolecules* 2007, 40, 3366-3372.
6. Cho, Y.; Lim, J.; Char, K. Layer-by-Layer Assembled Stimuli-Responsive Nanoporous Membranes. *Soft Matter* 2012, 8, 10271-1027.