Supporting Information for

Asymmetric Organic-Inorganic Membrane Formation via Block Copolymer-Nanoparticle Co-Assembly

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Outline

1, ISV synthesis and characterization

The ISVs were synthesized using living anionic polymerization following the procedures described in the literature.[1] The molar masses and polydispersities of the ISVs was determined using Waters 510 gel permeation chromatography (GPC) with a differential refractive index (RI) detector. The volume fraction of each block was calculated from NMR data obtained using a Varian INOVA 400 MHz ^{1}H solution nuclear magnetic resonance (^{1}H NMR) spectrometer with $CDCl_3$ (δ = 7.27 ppm) signal as an internal standard.

	f_{PI}	f_{PS}	f_{P4VP}	M_n (kg/mol)	PDI
ISV43	0.27	0.55	0.18	43	1.02
ISV91	0.32	0.55	0.13	91	1.20

Table S1. Volume fractions (*f*), molar masses (M_n), and polydispersities (PDI) of the two ISV triblock terpolymers used in this study.

2, Procedure for TiO_2 sol solution preparation

TiO_2 sol NPs were prepared by quickly adding through a septum 1.0 mL titanium tetraisopropoxide (97%, Sigma-Aldrich) into 0.312 mL HCl (37 wt%, Sigma-Aldrich) in a closed vial under vigorous stirring. The vial was kept closed and under stirring for 5 min before adding 3.0 mL anhydrous tetrahydrofuran (Sigma-Aldrich). After stirring this solution for 2 min, different amounts of sol solution were added to the ISV solutions.[2] TiO_2 concentration was estimated to be 0.76 mol/L in the sol solution, assuming a full conversion of TiO_2 precursor, and based on the volume of the solution after THF dilution.

3, Inorganic content in final membranes by TGA

Membranes were carefully transferred from the DI water bath and dried in air. A T.A. Instruments Q500 Thermogravimetric Analyzer (TGA) was used to analyze the retained inorganic content in the dried membranes. The TGA was under air atmosphere with a ramp rate of 10°C/min from room temperature to 560°C.

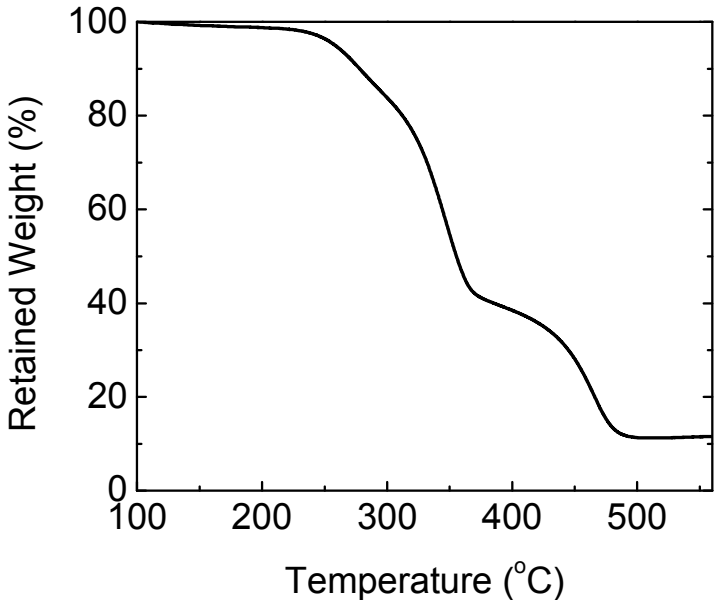

Fig. S1 TGA curve obtained from a dried hybrid membrane cast from an ISV43 with 11 wt% TiO_2 in the casting solution.

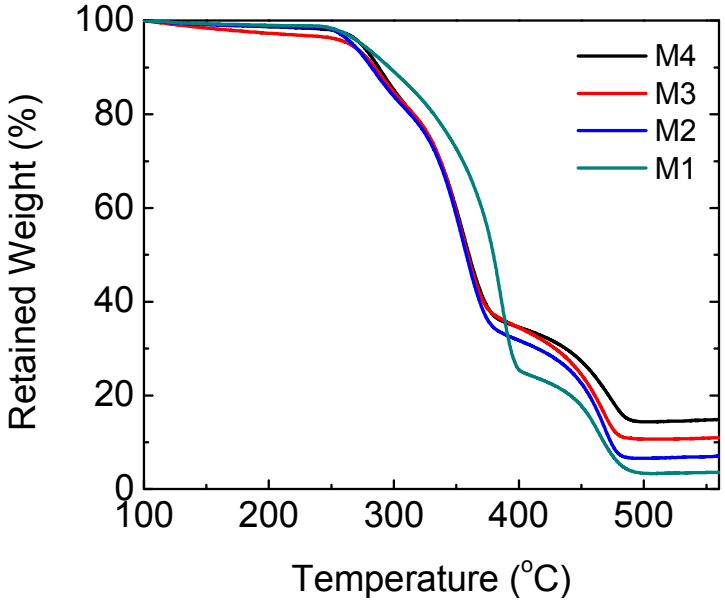

Fig. S2 TGA curves obtained from dried hybrid membranes cast from ISV91 (M1, M2, M3 and M4). The retained weights at 560 °C were 3 wt%, 7 wt%, 11 wt%, and 15 wt% for the four membranes M1 – M4, respectively.

4, SEM sample preparation and low-magnification SEM micrographs of membranes

SEM micrographs were acquired using a LEO 1550 ultrahigh resolution analytical field emission scanning electron microscope (FE-SEM) equipped with an in-lens detector. Samples were coated with Au-Pd for 10 sec prior to imaging using a Denton Vacuum Desk II sputter coater.

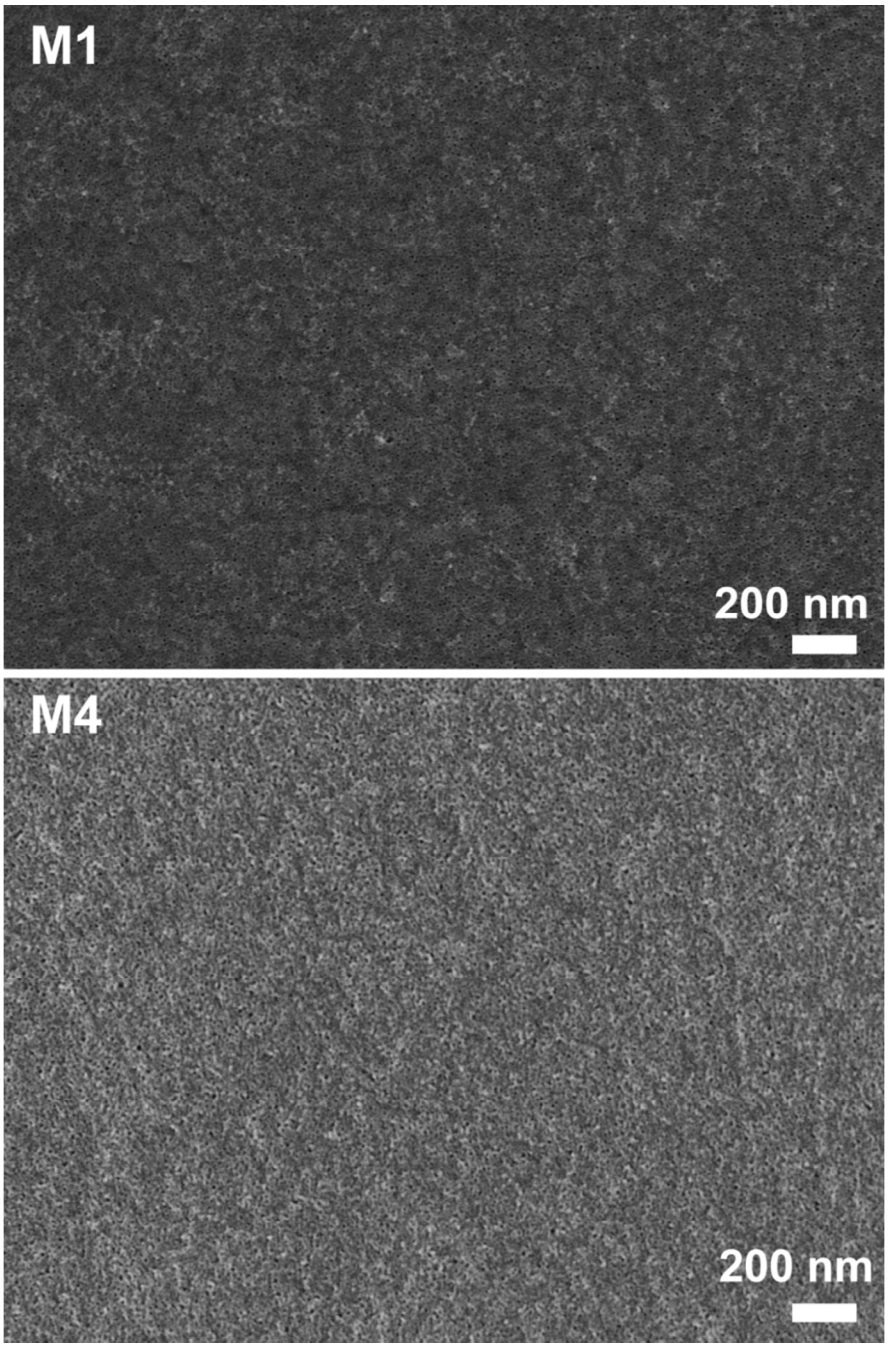

Fig. S3 SEM micrographs of large area top surfaces of M1 and M4.

5, Membrane performance tests

A stirred dead-end ultrafiltration test cell (Amicon 8010, Millipore, effective area 4.1 cm^2) was used in the water flux and solute rejection test. The cell was connected to a N_2 gas inlet and the pressure was monitored by an upstream digital gauge. The water (solute) height in the cell was kept constant for each test. During the test, the volume of solution transferred across the membrane was <10% of the total feed volume. The pressure resulting from the water (solute) mass was 0.03 psi and was added to the N_2 pressure shown on the gauge. For membrane performance experiments, ~1 mL of permeate was collected in a clean vial on a digital balance with the mass data collected by a computer every 5 – 12 sec. Pressure varied by ⌖0.01 psi over a given experiment.

The permeability of DI water in an ultrafiltration process was calculated from equation (1) shown below:

$$L_p = J_v / \Delta P \quad (1)$$

where J_v is the volumetric filtrate flux (volume flow rate per membrane area with the unit of m/s or $Lm^{-2}h^{-1}$) and ΔP is the trans-membrane pressure driving force.

PEO (Polymer Source Inc., Montreal, Quebec, Canada) solutions were all prepared at a concentration of 1g/L in DI water. The tests are conducted in a similar way as describe in the literature.[3] The PEO concentration in the feed and permeate was determined by an aqueous GPC (Waters Ambient Temperature) with a Waters 410 differential RI detector. The observed solute rejection was calculated from equation (2) as follows:

$$R_o = 1 - C_p / C_f \quad (2)$$

Where C_p and C_f are the concentration of solute in the permeate and feed, respectively.

6, Permeability analysis from the Hagen-Poiseuille equation

The Hagen-Poiseuille equation relates membrane permeability (L_p) with volumetric flux (J_v) and transmembrane pressure (Δp) to the membrane structure parameters as

$$L_p = \frac{J_V}{\Delta p} = \frac{\varepsilon \cdot r_{pore}^2}{8\mu \cdot \delta_m}$$

Where ε is the porosity, r_{pore} is the pore radius, μ is the viscosity of the liquid ($8.9 \diamond 10^{-4}$ Pa·s for water at 25°C), δ_m is the actual membrane thickness, $\delta_m = \tau \cdot l$ for tortuous pores, where τ is the tortuosity factor, usually 2-5 depending on the morphology, $\tau = 1$ for parallel cylindrical pores. l is the thickness.[4]

(1) Permeability estimation

From the rejection data of variously sized PEO molecules, a pore radius r_{pore} = 12.5 nm (d_{pore} = 25 nm) was estimated for M4. Since the morphology of the membrane M4 is network-like, the porosity and the thickness of the membrane separation layer are difficult to determine. We estimated a porosity ε = 0.1 and thickness $\delta_m = \tau \cdot l = 1.8 \diamond 100$ nm = 180 nm, resulting in a permeability of:

$L_p \sim 4000$ $Lm^{-2}h^{-1}bar^{-1}$

From this rough estimation, it is evident that a permeability of order thousands $Lm^{-2}h^{-1}bar^{-1}$ is reasonable for our organic-inorganic membranes.

(2) Structure factor (δ_m / ε) calculation

Assuming L_p = 3200 $Lm^{-2}h^{-1}bar^{-1}$, r_{pore} = 12.5 nm from the M4 membrane, the structure factor δ_m / ε was back calculated from Hagen-Poiseuille equation to be:

δ_m / ε = 2.5 μm

Reference

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2. Docampo, P.; Stefik, M.; Guldin, S.; Gunning, R.; Yufa, N. A.; Cai, N.; Wang, P.; Steiner, U.; Wiesner, U.; Snaith, H. J. *Adv. Energy Mater.* **2012,** 2, (6), 676-682.

3. Phillip, W. A.; O'Neill, B.; Rodwogin, M.; Hillmyer, M. A.; Cussler, E. L. *ACS Appl. Mater. Interfaces* **2010,** 2, (3), 847-853.

4. Zeman, L. J. Z., A. L., *Microfiltration and Ultrafiltration: Principles and Applications*. Marcel Dekker: New York: 1996.