Ordered lamellar hybrid membranes are of great interest, due to their application as functional materials, including molecular sieving, biosensors, optical devices, and drug, as well as gene deliveries, but their fabrication remains challenging because three critical issues regarding synthesis of regular nanosheets, interfacing, and their spatial distribution in a polymer matrix are difficult to address simultaneously. Here, we fabricated a well-defined hybrid lamellar membrane through one-pot self-assembly, whose structure consisted of alternating layers of hydrophilic hyperbranched poly(ether amine) (hPEA) and polyhedral oligomeric silsesquioxane (POSS). The POSS-capped photosensitive hPEA initially formed ultrathin sandwich-like hybrid nanosheets (HNS) with a thickness of $5 \pm 0.5$ nm in an aqueous solution through a living crystallization-driven self-assembly, which subsequently, generated a highly ordered lamellar hybrid membrane with a uniform layer of spacing through direct self-stacking by filtration. The resulting membrane acquired a well-defined lamellar structure, thereby providing an ideal model to study molecular diffusion in confined spaces. Also, it could be used for the separation of molecules of different sizes or charges in water solution and is capable of being efficiently, effectively, and economically (known as 3E) applied for the purification of products of methyl orange and fluorescein from their precursor mixtures. This one-pot assembly of the hybrid polymer provides a facile and essential alternative to fabricate highly ordered hybrid membranes.

Keywords: hybrid nanosheets, hybrid membrane, lamellar structure, molecule sieving, self-assembly

Introduction

Lamellar hybrid membranes, in which inorganic two-dimensional (2D) nanosheets are sheathed or decorated by a polymeric material, have recently gained remarkable interest and exhibited exceptional advantages in molecular sieving for the continuous operating mode of lamellar membranes, and the synergy of functional hybrid components (1+1>2). Hybrid membranes with layered configuration promise clear-cut sieving in size exclusion and continuum transportation for the narrow width distribution of tight confined sub-nanometer-scale...
2D channels of organic polymers, endowing selectivity property in molecular sieving. As a fundamental part of hybrid membranes, using high-aspect-ratio 2D nanosheets exhibit resultant exotic physicochemical properties, different from those of their isotropic counterparts due to their extended lateral dimensions and nanometer thickness. At present, high-performance hybrid lamellar membranes created using various 2D nanostructures, including metal-organic framework (MOF), zeolites, transition-metal dichalcogenides (XS2), graphenes, and graphene oxide (GO) could achieve molecular sieving properties. Their ability to form intrinsic porous structure or nanocapillaries/channels between individual layers exhibit inherent advantages in molecular sieving.

Although significant achievements have been made for hybrid membranes used in molecular sieving in the past few years, the realization of complex hybrid hierarchical structures implies a perfect integration of the chemistry and the process, which plays a central role in “integrative chemistry” in the field of advanced hybrid materials. However, during the fabrication of these lamellar hybrid membranes, three critical issues are inevitably considered when combining the organic and the inorganic aspects at the molecular or nanoscale levels in one material. First, regular nanosheets with controlled size, thickness, and shape are required and must qualify in forming ordered lamellar structures whose fabrication remains challenging. Potential defects might occur in membranes fabricated by detached sheets for shortcomings such as low-aspect-ratio, fragmentation, morphological defects, and reaggregation, accompanying the traditional top-down exfoliation process. Second, a spatially uniform distribution of inorganic nanosheets and polymers is critical for hybrid membranes employed in molecular transportation. Rapid permeation is well recognized to rely on continuous pore-flow transportation and ordered molecular flow through interlayer spaces. However, currently available hybrid lamellar membranes possess irregular channels generated by the heterogeneous distribution of nanosheets in polymeric matrices. Achieving a spatially uniform hybrid membrane with a settled thickness of organic or inorganic layers by direct incorporation 2D nanosheets or decorating with organic polymers is difficult. Third, the interfacial compatibility between polymers and inorganic nanosheets is an unavoidable issue in the hybrid membrane as it plays a predominant role in modulating properties such as separation and stability. The phase separation and inevitable slip of two components by simply incorporating 2D nanostructures with polymeric matrices during filtration might negatively affect the stability and mechanical properties of the physical blending with weak bond connections such as van der Waals forces, hydrogen bonds, or electrostatic bonds. Thus three critical issues of regular nanosheets fabrication are desirable, viz, interfacing, spatial distribution, and polymers that affect the performance of hybrid membranes, synergistically and cooperatively.

To address these critical issues, here, we developed a one-pot assembly strategy to fabricate a well-defined...
hybrid lamellar membrane by using a polyhedral oligomeric silsesquioxane (POSS) end-capped hyperbranched poly(ether amine) (POSS/TX-hPEA) as the building block (Scheme 1a), which initially, formed 2D hybrid nanosheets (HNS) through living crystallization-driven self-assembly (CDSA) in an aqueous solution. The uniform square HNS with a tunable size was sandwich-like and comprised hPEA as the outer layer and a POSS aggregation as the inner layer. The uniform sandwich-like nanosheets permit a unique construction of alternating organic-inorganic lamellar structure through a direct self-stacking process of filtration. Different from the reported hybrid membranes that POSS nanoparticles physically blended with polymer matrices, the HNS-M fabricated by HNS could avoid the mismatched interfacial compatibility effectively, as the hPEA layer is covalently bonded to the organic POSS at a molecular scale. In the stacking process, the photo-crosslinked and intertwined hPEA chains occupied the interlayer space of the POSS aggregation forming in-plane 2D nanochannels, thereby endowing the membrane with precise molecular sieving in the filtration process.

Results and Discussion

Preparation of POSS/TX-hPEA

The hPEA possesses a large number of secondary amino groups in the periphery (Supporting Information Figure S1b). Through the click reaction with POSS and TX, hPEA could be presented to the periphery to obtain amphiphilic hyperbranched poly(ether amine) (POSS/TX-hPEA).

Preparation of 2D hybrid HNS

We prepared a series of square HNS with a tunable size using the CDSA of amphiphilic hyperbranched polymer POSS/TX-hPEA, which comprised hydrophilic hPEA as the backbone and hydrophobic POSS and TX moieties in the inner core. A detailed description of the synthesis and characterization of the POSS/TX-hPEA are shown in Supporting Information Figures S1 and S2. The planar TX was photosensitive, and thus, could cross-link with the resulting HNS by UV light irradiation. Self-assembly was carried out by gradually adding water to a homogeneous 1,4-dioxane solution of POSS/TX-hPEA according to a previously reported method. AA filtered water, prepared using the AA nanofiltration system (Milli-Q gradient; Millipore, USA), was added, during which the solvent became progressively unsuitable for the hydrophobic POSS and TX moieties because of solubility differences among the hydrophilic hPEA and hydrophobic POSS and TX in water. Consequently, a microphase separation occurred when the water content reached a critical value. Induced by the crystal of the hydrophobic POSS and π–π stacking of the TX moieties, the core hydrophobic POSS and TX moieties aggregated and formed an inner hydrophobic layer along the x–y plane directed by the backbone hydrophilic hPEA, resulting in the generation of regular sandwich-like HNS (Scheme 1a).

The nanosheets obtained (Supporting Information Figure S3a-c) could well disperse in an aqueous solution with a hydrodynamic size of 812 nm and low the polydispersity index (PDI) of 0.24 (Supporting Information Figure S3d).
Figure S3e), determined by dynamic light scattering (DLS) using a 3D LS Spectrometer (PD2000DLS; Precision Detectors, Milpitas, CA, USA). The bright cyan fluorescence emission (Supporting Information Figure S3c) and the blue fluorescent image (Supporting Information Figure S3d) of the divided nanosheet ascribed to the fluorescence of the TX moieties on the hPEA backbone in the resulting nanosheets. The Tyndall effect (Supporting Information Figure S3b and Scheme 1b, inserted image) and the resultant Zeta potential (+37.5 ± 0.75 mV) of the homogenous solution indicated high stability of the HNS in an aqueous solution for covalent bonding between hard hydrophobic POSS and soft hydrophilic hPEA on the molecular scale. A series of HNS with regular square shapes, different sizes, and an average edge length of 0.5–2.5 μm were prepared using CDSA of the POSS/TX-hPEA and by controlling the CDSA time, revealed by transmission electron microscopy (TEM) (Scheme 1b and Supporting Information Figure S4). With regard to the size of the POSS (∼1 nm), and the molecular weight of the hPEA, uniform dispersion and thickness of 5 ± 0.5 nm were obtained (Scheme 1c and d), suggesting that the HNS was in monolayer form, in which the hydrophobic POSS and TX formed the inner layer, while the hydrophilic hPEA chains contacted with water to stabilize the assemblies. Accordingly, sandwich-like organic–inorganic 2D HNS with a high-aspect-ratio (∼460) in the extended lateral dimensions and nanometer (nm) thickness were fabricated successfully through CDSA. As Supporting Information Figure S4c shows, the selected area electron diffraction (SAED) pattern of the HNS obtained in Scheme 1 and Supporting Information Figure S4b (red dotted cycle) exhibited a diffraction ring corresponding to the interplanar spacing, d, of 1.17 nm along the z-axis, which bore the same size as that of the POSS nanoparticles. In other words, a sandwich-like ultrathin HNS, whose structure comprised a versatile hPEA as the outer layer on both sides and a POSS aggregation as the inner plane, was developed by the living CDSA of the hPEA-capped POSS.

Preparation and characterization of a hybrid HNS-based membrane (HNS-M)

An advantage of this uniform ultrathin nanosheet with a high-aspect-ratio is that it could be stacked layer-by-layer to form a lamellar membrane with a considerably enhanced transparency. The layer-stacked HNS-M was prepared using a vacuum-assisted filtration of the homogeneous HNS solution onto an anodized aluminum oxide (AAO; pore diameter = 0.22 μm) substrate (Scheme 1a). Contrary to the random stacking of nanosheets with narrow x-y planes (Supporting Information Figure S5a), no vertical nanosheets were found on the surface morphology after examination by atomic force microscopy (AFM; Fuzhou University, Fujian, China). The height and in-phase images for the direct volatilization of the HNS solution on mica plates are shown in Supporting Information Figure S5b–d, where the divided nanosheet is marked with green dotted lines. During filtration, HNS with micrometer lateral x-y widths and nanometer thickness regularly stacked along the z-axis, forming a self-standing transparent membrane (Scheme 1a), which exhibited a hydrophilic surface for the coverage of hPEA chains on the sandwich-like HNS, with a contact angle of ≈46° (Supporting Information Figure S6d). Upon exposure to UV light, TX moieties could extract hydrogen from hPEA backbones to produce radicals, likely to enhance the stability of the resulting cross-linked HNS-M through the coupling of the radicals (Supporting Information Figures S6a). After the asymmetric (as)-prepared membranes were irradiated using a UV light for 10 min, the intensity of the absorption peak of TX decreased substantially (Supporting Information Figure S6c), and the bright cyan fluorescence of the membranes weakened significantly (Supporting Information Figure S6b), suggesting photocrosslinking of the HNS-M had occurred.

Cross-sectional TEM and scanning electron microscopy (SEM) images of the HNS-M were analyzed to gain insight into their morphology (Figure 1a–d). The calculations of both the alternating thickness (∼5.4 nm) in the TEM image of the cross-section of the HNS-M and the corresponding interplanar spacing (d = 5.4 nm) were obtained by fast Fourier transformation (FFT) algorithm displayed as the middle two spots in Figure 1b, confirming the existence of a long-range, highly ordered, lamellar structure, comparable with the measured thickness (5 ± 0.5 nm) using AFM (Scheme 1c and d). For the high-magnification view in Figure 1d, the cross-sectional bright, darkfield, and the corresponding high-angle annular dark-field (HAADF) images of the HNS-M exhibited complementary sequences, indicating its lamellar structure. The dark arrays in the bright-field image showed the POSS layer, which corresponded with the bright arrays in both the dark-field and HAADF images (Figure 1d) for a larger atomic mass of Si (POSS cages) than of C (hPEA chains). The overview image of the silicon (Si) element mapping confirmed that the fabricated HNSs were homogeneous across the whole membrane, and Si was almost located in the layered stacking (Figure 1d). Therefore, we inferred that all the nanosheets were stacked together along the z-axis and oriented in the x-y plane of the membrane, resulting in an ordered lamellar membrane with alternating organic–inorganic layers. The highly aligned lamellar microstructures guaranteed a high light transmittance even with a thickness of 22.0 μm for a well-oriented POSS building block, which was conducive to decreasing the light scattered between the nanosheets (Scheme 1a, an optical photograph of the transparent HNS-M). Moreover, the modulus of the HNS-M was higher than that of the POSS/TX-hPEA solid.
(Supporting Information Figure S7) for this highly ordered structure, evidenced by the long-range ordered lamellar structure and a cross-sectional view of the SEM image (Figure 1c). Accordingly, the relatively high-aspect ratio between the edge length and thickness (\(\sim 460\)) of the resulting nanosheet produced a membrane with alternating organic–inorganic layered structures. Additionally, the high surface area coated with large amounts of functional hPEA polymer chains of the HNS led to the formation of numerous recognition sites in the 2D plane throughout the membrane for molecular sieving.

The structure of the HNS-M was investigated further using differential scanning calorimeter (DSC) and X-ray diffraction (XRD) (Supporting Information Figure S8). Two exothermic peaks in the DSC thermogram of pure POSS powder indicated the coexistence of its two crystalline phases, supported by the XRD data. On the contrary, only a single endothermic peak at the lower temperature of 120 °C and a lower enthalpy of melting (\(\Delta H_m\)) was observed for the HNS-M. This might be ascribed to the 2D crystallized aggregation of the POSS moieties in the ultrathin layer with a thickness of several nanometers in the HNS-M, which was confirmed by small-angle X-ray scattering (SAXS) measurements (Figure 1e). The distinct reflection peak at \(d\) spacing of 1.07 nm (Point II, \(q = 6.26 \text{ nm}^{-1}\); Figure 1e) was consistent with the fingerprints of POSS crystals (Supporting Information Figure S8c), indicating that the triangular pyramidal molecule of POSS/TX-hPEA took face-to-face assembly with the crystallized aggregation of the POSS in the middle layer, forming the sandwich-like HNS, thereby, resulting in an ordered lamellar HNS-M. The discrete scattering maxima located at \(q = 1.25 \text{ nm}^{-1}\) SAXS (Point I) of the HNS-M (Figure 1e) confirmed the existence of a long-range ordered structure. The corresponding \(d\) spacing of 5.0 nm was located in the HNS thickness, \(t\), range of \(5 \pm 0.5\) nm, determined by AFM (Scheme 1c and d), and was consistent with the interplanar spacing, \(d\), of 5.4 nm calculated by the corresponding FFT displayed in Figure 1b. Thus, concerning the size of the POSS nanoparticles, the HNS-M had a highly ordered lamellar structure comprising alternating POSS and hPEA layers whose structures are shown in Figure 2b.

**Water flux of the HNS-M**

The uniformed hydrophilic hPEA layer in the resulting lamellar hybrid membrane provided an ideal confined 2D nanochannel for molecular transportation, which is critical in the design of layered membranes for filtration and separation techniques for any unusual fundamental behavior that might arise at the molecular scale. Water fluxes (Figure 2a) were tested to evaluate the performance of hybrid HNS-M of different thicknesses. We observed a rapid exponential decrease in efficiency with increasing membrane thickness. Compared with classical flow equations, we employed the Hagen–Poiseuille eq (1) often used to describe the water flow between laminar...
membranes by assuming that water inside the 2D interlayer channels behaved as a classical liquid.\textsuperscript{22,33,34}

\[ J = \frac{(d^4 \Delta \rho)}{(12 \pi L^2 \eta h)} \]

where \(d\) is the vertical space between adjacent nanosheets, \(L\) the average lateral length of nanosheets, \(\eta\) the viscosity of water, and \(h\) the thickness of the lamellar membrane. Taking the thickest HNS-M (\(h = 22.0 \mu m\)) as an example, this equation yielded a flux of \(2.07 \times 10^{-6} \text{ L/(m}^2\text{·h)}\), which was \(10^4\) orders of magnitude smaller than our experimental value \([20.7 \pm 3.9 \text{ L/(m}^2\text{·h)}]\). One possible reason is the basic assumptions made in the Hagen-Poiseuille equation, which are those of the basic laminar flow and “no-slip” at the boundary layer (or liquid flow with zero velocity). The discrepancy between the experimental flux and this classical equation suggests that the velocity of water flow through the HNS was not equal to zero.\textsuperscript{22,34} Such a rapid transportation of water through confined 2D nanospaces was mainly ascribed to water rapidly occupying the hydrophilic interlayered area of nanosheets and the ordered hydrogen bonds formed by the single file of water molecules.\textsuperscript{35,36} resulting in uninterrupted and steady water-boned flow in the nanospaces. Similar phenomena were observed in the cases of carbon nanotubes (CNTs) with a diameter smaller than 10 nm, which indicated a flow enhancement of \(10^3\text{–}10^4\) fold for water transportation.\textsuperscript{33,37}

**Charge-selective separation of the HNS-M**

Based on the well-defined lamellar structure with 2D nanospaces and high water flux, we envisioned that the HNS-M might be a potential candidate for molecular sieving and separation, especially for the removal of water-soluble organic contaminants during water treatment.\textsuperscript{38} For example, dye molecules, mostly from textile, printing, and dye-manufacturing processes, are carcinogenic, mutagenic, and strenuous to biodegrade because of their complex aromatic structures.\textsuperscript{39} To evaluate the performance of a positively charged HNS-M in separating a series of organic pollutants, as well as its environmental significance, we chose several water-soluble organic dye molecules, both positively and negatively charged, to conduct filtration experiments. Specifically, we selected the following cell-permeant dyes: methyl blue (MB), Rhodamine 6G (Rho 6G), methyl orange (MO), Synchronator (SR), fluorescein (FR), and calcein (Cal). The van der Waals sizes of these dye molecules were calculated using Materials Studio 7.0 (Accelrys, San Diego, CA, USA), as shown in Figure 3a. UV–vis spectroscopy was used to check each dye concentration before and after the filtration process. For the negatively charged dyes with different sizes such as MO, SR, FR, and Cal, almost all of them were removed from the water after filtration (Figure 3d–g). In contrast, MB, with a similar size as MO but positively charged, exhibited no noticeable concentration change during the filtration process, and the test condition remained unchanged, which was confirmed by the optical photographs displayed as an inset in Figure 3b. The detailed separation data are summarized in Supporting Information Table S1 and Supporting Information Figure S9, with rejection rate entries of 98.1%, 87.7%, 99.8%, 98.3%, 5.6%, and 2.7% for MO, SR, FR, Cal, MB, and Rho 6G, respectively. Precisely, the HNS-M could separate negatively charged MO, SR, FR, and Cal from water, while the positively charged dyes (MB and Rho 6G) exhibited no noticeable concentration change during the separation tests. This distinct observation was due to the exhibited electrostatic interaction by the positively charged HNS-M, which enabled effective trapping of the negatively charged dyes (MO, SR, FR, and Cal) that caused partial blockage at the entrance of the 2D nanospaces of the laminar membranes, resulting in a narrowed space for the molecular dye transportation.

As Figure 2b shows, positively charged hPEA chains entwisted (blue entanglement lines) for the protonation of amino groups and occupied the interspace of the adjacent POSS layers (reddish-brown cubic). During
filtration under a pressure of one bar (~ 1 atm), hPEA chains transported or trapped molecules flowing along the interspace of polymer chains, while the cubic POSS acted as a directional guideline and blocked the layer by preventing the molecules from passing through vertically. Regarding the size of POSS nanoparticles and positively charged dyes (0.8–1.0 nm wide), estimated by a DMol3 calculation at Geometry Optimization using Material Studio 7.0, the effective nanospace within the HNS-M for transportation of molecules was estimated to be <1.0 nm. Here, the effect of electrostatic interactions between the charged dyes and the positively charged groups of hPEA could not be ignored. Owing to the electrostatic interactions, the positively charged hPEA chains trap the negatively charged MO, SR, FR, and Cal molecules efficiently. As all the positively charged amino moieties were located at the backbone of the hPEA, which occupied the whole interspace of the POSS layer, the entrance would be narrowed adequately by the passage of negatively charged dye molecules (the smallest 3D size of >0.5 nm). Thus, the transportation of all negatively charged dyes was forbidden significantly by the blocked interspace of the swaying hPEA chains.

In addition, further filtration tests were conducted to obtain insights into the mechanism of the separation process for the amphiphilic hPEA, suggested a unique selective adsorption behavior toward both azo and fluorescent dyes in an aqueous solution. Taking the azo dyes of MO and Fluorescein dyes of FR and Cal, and other dyes of MB and Rho 6G. The concentration of different sized and charged organic dye in feed, permeate 50 mL and permeate 100 mL, as evidenced by the UV–vis spectra and insert optical photographs during filtration, (b) MB, (c) Rho 6G, (d) MO, (e) SR, (f) FR, and (g) Cal.

Figure 3 | Dye molecules model and rejection performance of the HNS-M. (a) Molecular model calculated from Material Studio 7.0, displayed inline, stick, ball and stick, space-filling spheres (CPK style; gray, carbon; white, hydrogen; yellow, sulfur; red, oxygen; blue, nitrogen) and corresponding chemical structure of the molecules of each dye, specifically, azo dyes of MO and SR, fluorescent dyes of FR and Cal, and other dyes of MB and Rho 6G. The concentration of different sized and charged organic dye in feed, permeate 50 mL and permeate 100 mL, as evidenced by the UV–vis spectra and insert optical photographs during filtration, (b) MB, (c) Rho 6G, (d) MO, (e) SR, (f) FR, and (g) Cal.
Size-dependent sieving of the HNS-M

Molecular selectivity is a critical parameter to determine the potential applications of filtration membranes. By considering a positively charged HNS-M and a highly ordered lamellar structure, we used several negatively charged organic molecules with different sizes as probes to evaluate the effectiveness of the size separation of HNS-M; specifically, the filtration was conducted with the corresponding precursor sodium sulfanilate (SSN) and resorcinol of the MO and FR dye molecules, respectively (Figure 4a and 4d), followed by tracing using UV-vis spectra. Although we obtained higher concentration of the retentate of MO and FR (Supporting Information Figure S10c and f), no noticeable concentration change was observed with SSN and resorcinol, meaning that the interspace generated by the swing of hPEA chains was larger than the size of the SSN and resorcinol (Supporting Information Figure S10b and e).

Accordingly, we performed filtration tests for the mixtures, SSN-MO, and resorcinol-FR. As Figure 4b and 4e shows, only traces in the filtrate of MO and FR were obtained, suggesting that high concentration remained as retentate, while SSN and resorcinol exhibited no remarkable change in concentration of both the retentate and the filtrate, based on our UV-vis spectra data of the filtrate and the mixture solution. Also, almost no color was observed with the permeation solution (Figure 4c and 4f). Moreover, some dye precipitates were visible to the naked eye with the ultrafiltration substrate, collected by drying the eluent (Figure 4c and 4f). Collectively, our results show that the HNS-M could be used to separate products from a reaction mixture, verified the selective rejection performance of the HNS-M to the mixed precursor-dye molecules. Additionally, HNS-M fixed the interspace generated by the swing of hPEA chains larger than 0.67 nm (the particle size of SSN and resorcinol was approximately 0.67 nm). Compared with the recrystallization or the extraction performed in product purification during the synthesis of MO and FR, this size-selective rejection membrane approach demonstrated efficiency, reliability, and a cost-effective method of product purification. Further, the HNS-M exhibited significant stability, recyclability, and sustained high filtration efficiency (rejection > 99%) for MO, even after five filtration cycles (Supporting Information Figure S11).

The superior rejection performance of the HNS-M is attributable to its much longer, and selective routes for molecule transportation, compared with the lamellar membranes formed using straight pore with the inner wall functionalized or fabricated by the 2D nanosheets (e.g., graphene oxide), and with functional groups.

Figure 4 | Size-dependent filtration for molecular sieving of dyes and their precursors. Synthetic routes of MO and FR from their precursor SSN (a) and resorcinol (d). UV–Vis spectra corresponding to the selective rejection of MO from a mixture of MO and its precursor SSN (b), and optical photographs of molecular sieving of MO-SSN mixed aqueous solution, collected solid dye by drying the eluent of ultrafiltration substrate where some solid dye precipitated (c); UV–Vis spectra corresponding to the selective rejection of FR from a mixture of FR and its precursor resorcinol (e), and optical photographs of the molecular sieving of the FR-resorcinol mixed aqueous solution, collected solid dye by drying the eluent of ultrafiltration substrate where some solid dyes precipitated (f).
located at the edges of each nanosheet. As Figure 2b shows, ideal vertical spaces between the adjacent nanosheets should lay precisely in the middle of the next layer to represent an equal probability of molecules to pass through all these branched points by moving either left (red dotted line) or right (red line). Taking the thickness of HNS-M as 22 μm into consideration, the average edge length and the thickness of the HNS were 2.5 μm and 5.4 nm, respectively. Thus, there were approximately 4074 layers in fabricating a 22 μm thick HNS-M. Accordingly, during filtration, ~ 5092 μm was the minimum length for each molecule to pass through, which was ~ 231 times longer than the thickness of the membranes. Positively charged hPEA chains were in the outer layer of the sandwich-like nanosheets and occupied the whole interspace between divided nanosheets. The selective route for molecule transportation elongated to at least ~ 231 times. That means, as observed through GPC, the extended passing routes enhanced considerably, the selective rejection of the HNS-M, based on a molecular charge while the selective rejection mechanism of GPC was based on molecular weight.

Accordingly, three aspects contributed to the excellent flux and separation performance of the HNS-M membranes. First, the hydrophilic surface of HNS-M benefited water gathering and permeation. Second, the HNS-M contained regular 2D HNS with a high-aspect-ratio (~460, Scheme 1b–d) and could generate a well-defined and straight interspace (Figure 1) between adjacent POSS layers for molecules to pass through. Hence, the thickness of the HNS-M increased, the solutes passed through a longer route (~231 times longer than the intrinsic thickness of the membrane, 22 μm; Figure 2), somewhat decreasing the corresponding permeance but increasing the separation property. Moreover, the high coverage of functional polymers of the positively charged hPEA on the surface of the nanosheets enhanced the charge-selective rejection of the membranes (Figure 3). In other words, the high-aspect-ratio and surface functional coverage of 2D the nanosheets contributed to the high flux and selective separation properties, respectively. Third, the interspace between the divided POSS layer was occupied by covalent bonding and stable hPEA-capped POSS. This strategy eliminating the mismatched interfacial compatibility between the polymer and inorganic POSS for covalent-bonded connection in precise molecular-level design. Via a direct self-stacking filtration, the sandwich-like nanosheets stacked into a well-defined and ordered lamellar structure with alternating hydrophobic POSS layers aggregating in the core and the hydrophilic hPEA chains occupying the periphery. Fixed and positively charged 2D nanochannels in the plane, generated by the polymer chains, endowed the membranes with precise molecular sieving based on charge and size. The high coverage of functional polymers of the positively charged hPEA on the surface of nanosheets elongated the transport route for each molecule to pass through and enhanced the selectivity of the products from the dye mixture molecules and their precursors, making it one of the best choices in purifying products in an efficient, effective, and economical manner (3E). This bottom-up strategy, based on the self-assembly of hybrid polymers, provides a vital alternative to fabricate well-defined lamellar hybrid membranes with high-potential in molecular separation or sieving.

Conclusion
We have demonstrated the performance of a highly ordered lamellar hybrid membrane fabricated through the one-pot self-assembly of hybrid hyperbranched poly(ether amine) (POSS/TX-hPEA). A uniform square HNS with tunable size and the sandwich-like structure was fabricated using CDSA with pyramidal molecules of hPEA-capped POSS. This strategy eliminated the mismatched interfacial compatibility between the polymer and inorganic POSS for covalent-bonded connection in precise molecular-level design. Via a direct self-stacking filtration, the sandwich-like nanosheets stacked into a well-defined and ordered lamellar structure with alternating hydrophobic POSS layers aggregating in the core and the hydrophilic hPEA chains occupying the periphery. Fixed and positively charged 2D nanochannels in the plane, generated by the polymer chains, endowed the membranes with precise molecular sieving based on charge and size. The high coverage of functional polymers of the positively charged hPEA on the surface of nanosheets elongated the transport route for each molecule to pass through and enhanced the selectivity of the products from the dye mixture molecules and their precursors, making it one of the best choices in purifying products in an efficient, effective, and economical manner (3E). This bottom-up strategy, based on the self-assembly of hybrid polymers, provides a vital alternative to fabricate well-defined lamellar hybrid membranes with high-potential in molecular separation or sieving.

Supporting Information
Supporting information is available.

Conflict of Interest
There is no conflict of interest to report.

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