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# Star polymer-assembled thin film composite membranes with high separation performance and low fouling

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## ABSTRACT

Thin film composite (TFC) membranes have attracted intense interest due to applications in various molecular separation processes including water purification, gas separation, organic solvent separation and saline-gradient energy production. In particular, growing global demands for clean water and reduced energy consumption have raised interest in highly permselective and low fouling TFC membranes for water treatment and desalination. This drive has led to the design of new molecular structures of TFC membranes using advanced materials. Here, we designed a new building block material, a star-shaped polymer, which can be assembled into the selective layer of the TFC membrane via a commercial interfacial polymerization (IP) technique. This ideal 3-dimensional compact globular geometry along with high density end-functional groups enabled the realization of membranes with higher permselectivity as well as superior antifouling properties even compared to commercial membranes. We demonstrate the remarkable versatility of this building block by using the same starting materials to fabricate membranes that can function either as nanofiltration or reverse osmosis membrane depending on the IP process conditions, which is not feasible with the conventional materials used in membrane fabrication.

## 1. Introduction

With the growing global concerns on water scarcity, environmental pollution and energy depletion, thin film composite (TFC) membranes have attracted intensive interest due to their applicability in water treatment, desalination, organic solvent separation, gas separation and sustainable energy production [1–4]. For instance, the state-of-the-art commercial reverse osmosis (RO) and nanofiltration (NF) membranes for water purification and desalination adopt a polyamide (PA) TFC structure consisting of an ultrathin selective PA layer on top of a porous support, where the selective layer governs separation performance [5]. The PA layer is formed by interfacial polymerization (IP) of a diamine monomer (*m*-phenylenediamine (MPD) for RO or piperazine (PIP) for NF) with trimesoyl chloride (TMC), which produced semi-aromatic or fully-aromatic cross-linked PA networks, respectively [1,6,7].

Despite great advances in TFC membrane development, there remains a strong demand for the membranes with high permselectivity and low fouling propensity that can reduce energy consumption in clean water production [7–9]. Unfortunately, efforts to enhance

membrane performance and/or fouling resistance by modifying the membrane surface and using additives/nanoparticles have proven to be marginal due to the intrinsic permeability-selectivity and performance-fouling trade-offs, which are imposed by the limited chemistry of the conventional PA layer [7–10].

Recent efforts to overcome these limitations have been dedicated to designing the molecular architecture of the selective layers using new materials and chemistries, including liquid crystals [11], proteins [12] and nanoparticles [13]. Although pioneering works on the membrane formation using these novel materials have demonstrated the potential of achieving high flux performance, antifouling function and high salt rejection applicable to high quality water production cannot be guaranteed.

Branched macromolecules (BMs) such as hyperbranched polymers and dendrimers have recently gained great attention as building materials of the selective layer because of their unique structures, high density terminal functional groups and large intramolecular free volume, which enables the creation of highly permeable polymer networks [10,14,15]. Additionally, the available functional groups can be utilized to impart antifouling function when membranes are modified

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