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# *In-situ* Preparation of Hydrophilic and Hydrophobic Nanodomains in Covalent Organic Framework Membranes for Ultrahigh Separation of Dyes from Aqueous Solution

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## Abstract

Covalent organic frameworks (COFs) membranes are highly efficient nano-filters for water purification due to their molecular size selectivity and tunable functionality. For membrane applications, it is essential to fabricate membranes that combine both excellent dye rejection and ultrahigh water permeability. In this study, we synthesized a novel COF membrane, TUS-46, which simultaneously satisfies these two conditions by precisely designing the pore channel metrics and environment using a stoichiometric imbalance method. The resulting TUS-46 membrane exhibited high dye removal (96%) and excellent water permeability (57.8 L $m^{-2}$ $h^{-1}$ $bar^{-1}$). The remarkable water permeability of the TUS-46 membrane was attributed to the two types of pores, the hydrophilic pores with unreacted aldehyde groups contributing to water adsorption and the non-hydrophilic pores to faster water diffusion.

## 1. Introduction

COFs demonstrate high crystallinity, excellent stability, and molecular-level designability, and in recent years, have been extensively investigated in diverse applications due to these characteristics.1), 2) COF membranes grown on substrates can be highly competent water nano-filters owing to their tunable functionality and molecular size selectivity. Regarding membrane applications, it is desirable to fabricate membranes with both high dye removal rates and excellent water permeability. In this study, we synthesized a novel COF membrane, TUS-46, which satisfies both of these conditions simultaneously by precisely designing the pore size using the unbalanced stoichiometry.

## 2. Experiment

TUS-46 was synthesized under solvothermal conditions by acid-catalyzed Schiff base formation reaction of two different linkers hexa(4-formylphenyl)benzene and 5,10,15,20-tetrakis(4-aminophenyl)porphyrin. Two different linkers, n-butanol, and acetic acid were added to frozen ampoule tubes and heated at 120 °C for 3 days. TUS-46 membrane was synthesized as follows: Surface-modified polyvinylidene fluoride membrane was synthesized by treatment in sodium hydroxide solution and 1.5% (3-aminopropyl)triethoxysilane. Linkers, solvent, and PVDF membrane were added to an autoclave reaction vessel and heated at 120 °C for 3 days. The resulting TUS-46 membranes were observed by scanning electron microscopy (SEM) and evaluated for dye separation ability.

## 3. Results and discussion

Specific surface area/pore distribution measurements revealed that the product obtained by the unbalanced stoichiometry had a high specific surface area of 637.7 $m^2$ $g^{-1}$ and was composed of pores of different sizes (5.89 and 8.04 Å). The TUS-46 membrane was evaluated for dye separation that showed a high dye rejection of 96% owing to the molecular sieving property of these pores, which discriminate between the dye methyl blue (23.6×17.4 Å) and water molecules (2.7 Å) (Fig. 1). Furthermore, zeta potential measurements revealed that electrostatic repulsion between the anionic methyl blue dye and the negatively charged surface of the TUS-46 membrane has contributed to the dye removal performance of the TUS-46 membrane. Besides, the TUS-46 membrane exhibited superior water permeability (57.8 L $m^{-2}$ $h^{-1}$ $bar^{-1}$) compared to similar COF membrane without the characteristic hydrophilic pores (5.89 Å) arising from unreacted aldehyde groups (Fig. 1). Hydrogen bonding interactions between water molecules and COFs were explored by density functional theory simulations. The results suggest that two water molecules are adsorbed between two residual aldehyde groups in the hydrophilic pore with a strong hydrogen bond. On the other hand, the 8.04 Å pore was interpreted as a hydrophobic pore, functioning as a low-friction fast diffusion pathway for water. Thus, we conclude that TUS-46 membranes exhibit high dye removal rates and excellent water permeability due to the coexistence of hydrophilic and hydrophobic pores within the COF structure (Fig. 2).$^{3)}$

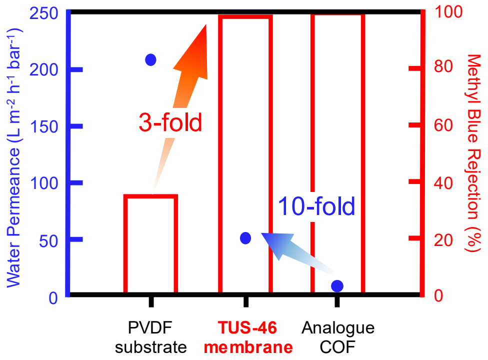

Fig. 1 Water permeance (blue) and methyl blue rejection (red) of PVDF substrate, TUS-46 membrane and analogue COF membrane

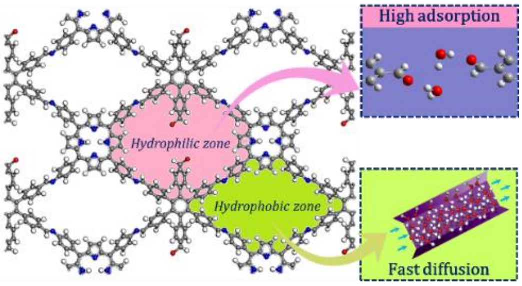

Fig. 2 Co-existence of hydrophilic and hydrophobic domains in TUS-46 membrane

## 4. Conclusions

A COF membrane with both excellent dye removal and water permeability was successfully prepared by the unbalanced stoichiometry approach. Characterization experiments revealed that the high dye removal rate of the TUS-46 membrane is due to the synergistic effects of molecular sieving and electrostatic repulsion in the COF pores. Furthermore, a comparison with analogous COF without unreacted aldehyde functionalities attributed the high-water permeability of TUS-46 membranes to the hydrophilic pores with unreacted aldehyde groups.

## References

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