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Mussel-Inspired Polydopamine Chemistry to Modulate Template Synthesis of 1D Metal-Organic Framework Superstructures

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Metal-organic frameworks (MOFs) are a class of fascinating crystalline hybrid materials with ordered three-dimensional structures constructed through the formation of coordination bonds between metal ions/clusters as nodes and organic ligands as linkers. Open framework structures and diverse functional groups in ligands, such as amino and carbonyl, offer large specific surface area and task-specific designability, making MOFs emerge as a type of porous material with significant prospects for application in many fields, including gas adsorption, catalysis, environmental remediation, etc.

While substantial efforts have been devoted to the synthesis of new MOFs and the exploration of their new applications in the past decade, developing synthetic strategies for controllable fabrication of zero-, one-, two-, or three-dimensional MOF architectures is a burgeoning area attracting escalating attention. In particular, assembling MOF crystals into one-dimensional (1D) superstructures not only provides a bridge between the nanoscale regime and meso- or macroscale objects, but also holds great potential for applications in gas adsorption, sensing, and optoelectronics. Albeit composite 1D porous superstructures supported by specific organic or inorganic substrates have been reported previously, especially those with tailor-made hollow structures, have been rarely achieved.

Among the methodologies for building 1D MOF superstructures, macro-structural template (hard template) synthesis represents one of the facile yet versatile synthetic approaches. However, given that the formation of MOFs occurs in the reaction solution, very few crystals can be anchored to the surfaces and/or channels of native substrates thereby failing to form well-defined 1D superstructures, especially for the inert templates with complicated structural features. To overcome this limitation, seeds coating or surface modification is usually required to promote the heterogeneous nucleation of MOF crystals. In this regard, a dynamic step-by-step method on anodic aluminum oxide (AAO) was proposed to confined the nucleation and growth of MOF crystals within the template system. However, due to the weak interaction between the inert surface of AAO and MOF nucleus, the MOFs in the channels were prone to accumulate on both sides of AAO and block the porous channels, making it difficult to form continuous 1D MOF superstructures spanning the whole channels.

Mussel-inspired polydopamine (PDA) chemistry, since the pioneering work of Messersmith in 2007, has received considerable attention as a versatile surface modification technique. Taking advantage of the self-polymerization of dopamine under aerobic and alkaline condition, the generated PDA nanoparticles can be homogeneously deposited to virtually any surface, forming a tightly adhesive layer. Moreover, the existence of abundant functional groups such as catechol and amine in PDA makes it an ideal platform to coordinate metal ions. This can provide nucleation sites and anchor bars to accommodate MOF crystals on inert surfaces, facilitating the construction of 1D MOF architectures in diverse templates.

Herein, we report, for the first time, the PDA chemistry modulated controllable synthesis of 1D MOF superstructures...
using a facile contra-diffusion synthetic strategy (Scheme 1) in the uniform cylindrical pores of polymeric membranes prepared by track-etched technique. It is highlighted that the heterogeneous nucleation and growth behaviors of MOF crystals can be tuned by altering the surface chemistry of the pore channels. Within the pore channels of the native polycarbonate (PC) membrane, a catalytic transesterification mechanism was revealed which led to the activation of the imidazole ligands to promote the nucleation of ZIF-8 crystals. In particular, taking advantage of the bio-inspired PDA chemistry, surface engineering of the pore channels was achieved, which greatly improved the controllability of the template synthesis of 1D MOF superstructures with enhanced structural stability, facilitating the formation of well-defined 1D ZIF-8 nanotubes spanning across the template channels with an aspect ratio up to 40. This strategy can be readily extended to the synthesis of other 1D MOF superstructures, such as ZIF-67, ZIF-12, and HKUST-1. Moreover, the obtained ZIF-8 composite membrane could efficiently separate organic dye contaminants in a simple flow-through mode.

Experimental
Materials
Sodium hydroxide (98%), zinc nitrate hexahydrate (99.5%), copper nitrate trihydrate (99.5%), cobalt nitrate (99%), ethyl acetate (99%, AR), and dichloromethane (99.5%, AR) were bought from Beijing Chemical Works. Dopamine hydrochloride (DA, 98%), methanol (99.9%, ACS/HPLC certified), ethanol (99.9%, ACS/HPLC certified), 1,3,5-benzenetricarboxylic acid (99%), 2-methylimidazole (99%), benzimidazole (98%) were supplied by J&K Scientific Co., Ltd. Tris (hydroxymethyl) aminomethane (Tris) (>99%), methylene blue (>95%) were purchased from Sigma-Aldrich. Deionized water was used for the preparation of all aqueous solutions. All reagents were used as received without further purification. Polycarbonate (PC) membrane was purchased from Bayer Company.

Preparation of PCTM
The polycarbonate track-etched membranes (PCTM) were prepared according to our previously reported method. Firstly, PC membranes with a thickness of 10 μm were irradiated by Kr84 ions on heavy ion accelerator at normal incidence. After exposure to ultraviolet (UV) light for 1 hour on each side, the sensitized membranes were fixed on a mould and immersed in 6.25 mol/L NaOH aqueous solution at 50 °C for 10 min. After chemical etching, the obtained PCTM were rinsed for three times by deionized water under ultrasonication and then dried at room temperature.

Modification of PCTM via PDA deposition
A piece of as-prepared PCTM was fixed on a mould and washed by deionized water, followed by the immersion into 10 mM Tris-HCl (pH=8.5) buffer. After vacuum treatment for 30 min to exclude the air in the pores, dopamine hydrochloride solution was added dropwise into the buffer under mechanical and magnetic stirring (200 rpm) on both side of PCTM (Fig. S1). The total concentration of dopamine hydrochloride in buffer was 1 g/L and the deposition process lasted for 8 hours at room temperature. Then, the PDA modified PCTM was rinsed by deionized water under ultrasonication and then dried in vacuum oven at 50 °C.

Contra-diffusion synthesis of MOFs within PCTM pore channels
A series of MOFs including ZIF-8, HKUST-1, ZIF-67, and ZIF-12 were synthesized within the pore channels of the PDA modified PCTM via a contra-diffusion method. Taking the template
synthesis of ZIF-8 as an example, zinc nitrate hexahydrate (297 mg, 1 mmol) and 2-methylimidazole (328 mg, 4 mmol) were dissolved in 20 mL methanol, respectively. A piece of PDA modified PCTM was then immersed in the zinc nitrate/methanol solution for 30 min following by a slight dipping in methanol, enabling the pre-coordination of Zn\textsuperscript{2+} with the PDA coating. After that, the PCTM was mounted between the two chambers of a contra-diffusion cell. And, zinc nitrate solution and 2-methylimidazole solution were synchronously added into different chamber. After one hour, the functionalized PCTM was dipped in methanol several times to wash off the loose crystals on the surface and dried under vacuum at 50 °C. The digital photo of the reaction setup is shown in Fig. S2. For control experiments, a piece of pristine PCTM without PDA modification of the pore channels was employed for contra-diffusion synthesis of 1D MOFs according to the same recipe described above. For the synthesis of other MOFs, all the ZIFs were synthesized by same molar concentration of precursor solution. But for HKUST-1, 1 mmol copper nitrate trihydrate (241 mg) and 1.33 mmol 1,3,5-benzenetricarboxylic acid (280 mg) were used to prepare the precursor solution. To obtain 1D superstructure of the MOFs, the membrane templates were dissolved in dichloromethane. Self-supported 1D MOF superstructures were collected by centrifuging, followed by repeated washing in methanol and dried under vacuum at 50°C.

Separation performance of organic dyes

The separation performance to remove methylene blue from aqueous solution was demonstrated in a filtration mode using the ZIF-8 functionalized PCTM. A piece of ZIF-8 functionalized PCTM was fixed in a membrane vacuum filtration apparatus. 3 mL methylene blue solution (5 mg/L) was introduced to the apparatus at room temperature. The solution passed through the functionalized PCTM assisted by a vacuum pump (vacuum degree ~ 0.09 MPa) at a flow rate of ~ 3 mL/min. The concentrations of the original methylene blue solution and the filtrates were also determined by UV-vis spectrometry.

Characterizations

Scanning electron microscope (SEM) was conducted by using ZEISS MERLIN and FEI QUANTA 200 scanning electron microscope. The sample was disposed with metal or carbon spray before observation. It was observed at an accelerating voltage of 30 kV in vacuum condition after metal sprayling. Transmission electron microscopy (TEM) images were recorded by using a model H-7700 microscope with an accelerating voltage of 120 kV. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet i10 Infrared Microscope. Powder X-ray diffraction (XRD) patterns were obtained on a diffractometer with Cu Kα radiation, with a scan step of 0.2° and the scan range between 3° and 50°. Nitrogen adsorption-desorption isotherms were measured by a NOVA 3200e Surface Area & Pore Size Analyzer. Samples were dried at 80 °C (for PCTM) or 120 °C (for nanotubes) under vacuum for at least 3 h before the nitrogen adsorption experiments. Specific surface areas were calculated based upon the Brunauer-Emmett-Teller (BET) method. UV-vis spectra between 200 and 800 nm were recorded at room temperature with a Cary6000i spectrometer using a 1-cm path length quartz cuvette. Thermogravimetric analysis (TGA) was conducted on a TA Instruments SDT Q600 with a heating rate of 10 °C/min from 30 °C to 900 °C. Samples weighing between 10 and 20 mg were heated in N\textsubscript{2} flow (100 mL/min).

Results and discussion

To study the nucleation and growth behavior of MOF crystals within the confined microchannels of polycarbonate track-etched membrane (PCTM), two classes of MOFs with different crystalline structures, i.e., ZIF-8 and HKUST-1, were chosen as prototypes due to their structural stability and mild synthesis compatible with the polymeric templates. The former is made by zinc ions coordinated by four imidazolate rings with pore aperture of ca. 3.4 Å, while the latter, made up of copper paddlewheel nodes with 1,3,5-benzenetricarboxylate (BTC) struts, is featured by three distinct internal pores (two of comparable size, ca. 14 Å, and a smaller pore ca. 10 Å) (Fig. S3).\textsuperscript{4,5} The surface and section morphologies of pristine PCTM under SEM are shown in Fig. 1a and Fig. 1b. Cylindrical pore channels with a diameter of 260 nm were observed spanning across the whole thickness of the membrane. The inset in Fig. 1a shows the digital photo of a native PCTM.

In a contra-diffusion synthesis, a piece of PCTM was employed to separate the two chambers containing the solutions of metal ions and ligands (Fig. S2). The concentration gradient driven diffusion across the PCTM, resulting in the nucleation and growth of MOF crystals within the pore channels. The SEM section view in Fig. 1c shows that a large number of ZIF-8 crystals were formed inside the pore channels. After dissolving the template, well-defined hollow 1D ZIF-8 superstructures constructed by intergrown crystal nanoparticles were obtained (Fig. 1e). The 1D ZIF-8 superstructure replicated the dimensional features of the pore channels. XRD analysis confirmed the ZIF-8 structure generated in the PCTM template and isolated 1D superstructures, which was consistent with the conventional ZIF-8 crystals (Fig. S4). Selected area electron diffraction analysis (Fig. 1e, inset) suggested the polycrystalline nature of the ZIF-8 superstructure. For the case of HKUST-1, however, only a few intergrown nanocrystal were found at the entrances of the pore channels (Fig. 1d). After template removal, solid HKUST-1 nanorods less than 1 μm were obtained (Fig. 1f), suggesting a limited diffusion path of the ligands during the synthesis. This may be attributed to the relatively larger size of the HKUST-1 crystals under the experimental conditions (Fig. S5), blocking the pore entrances and preventing the further diffusion of the ligands.

Meanwhile, a more careful examination of the 1D ZIF-8 superstructures shows a continuous growth of the ZIF crystals along the pore walls with clearly resolved thick boundaries (Fig. 1e), which implies the potential influence of the surface chemistry of the polycarbonate templates on the nucleation and growth of the ZIF-8 crystals. It is known that imidazole...
compounds can catalyze transesterification reactions.\textsuperscript{56-58} Hence we speculated that, for the template synthesis of ZIF-8 on PCTMs, the interaction between the imidazole ligands and the polycarbonate matrix might play an important role in the crystallization process of the ZIF-8 crystals. To verify this point, solvent synthesis of ZIF-8 with the introduction of ethyl acetate as nucleation agent was performed. The digital photo in Fig. 2a records the synthesis of ZIF-8 catalyzed by different additions of ethyl acetate. Apparently, a higher dosage of ethyl acetate resulted in a faster crystallization rate of ZIF-8. Meanwhile, an evident decrease of the average particle size from 98 nm to 23 nm was observed under TEM (Fig. 2b-2d), suggesting the promotion of nucleation rate with the aid of ethyl acetate.\textsuperscript{62}

In a typical synthesis of ZIF-8, the formation of 2-methylimidazole (mIM) anions via deprotonation is basically a key step to promote the nucleation and growth of ZIF-8 crystals.\textsuperscript{53} Upon contact with ester compounds, mIM ligands can catalyze a transesterification reaction according to an established mechanism shown in Fig. 3. The catalytic cycle results in the generation of deprotonated mIM ligands. This is expected to activate the coordination between the mIM ligands and the metal ions. Such an understanding helps to elucidate the nucleation and growth behavior of MOF crystals in the pore channels of PCTM. For the template synthesis of ZIF-8, the mIM ligands diffuse into the pore channels and catalyze the transesterification reaction of polycarbonate, which generates a relatively high concentration of activated mIM ligands, thereby inducing the preferential nucleation and growth of ZIF-8 crystals adherent to the pore walls without blocking the channels. Therefore, after removing the template, hollow 1D ZIF-8 superstructures with thick boundaries were obtained. It is worth mentioning that the imidazole-catalyzed transesterification reaction can be also proven by the mechanical strength change of the polycarbonate membrane. After 3 h contra-diffusion synthesis, the polycarbonate membrane exhibited a sharp decrease in the mechanical strength and a fragile composite membrane was finally synthesized.
obtained after 6 h (Fig. S6). In contrast, due to the poor interaction between the BTC ligands and the polycarbonate, matrix, the growth of HKUST-1 crystals was not confined to the surfaces of the pore walls. The large-sized HKUST-1 crystals accumulated at the entrance of the pores, preventing the continuous diffusion of BTC ligands into the channels. Thus, only short HKUST-1 nanorods were obtained after removing the PCTM templates.

Although the surface directed growth of ZIF-8 realized the preparation of hollow 1D MOF superstructures, the relatively large crystal size with non-uniform stacking did not provide ideal channels with homogeneous inner diameter. Due to the poor interfacial strength, cracks and fractures were often found for the isolated 1D ZIF-8 superstructures (Fig. S7). Furthermore, as mentioned above, the sacrifice of membrane strength also hindered the fabrication of a robust composite membrane for separation applications. To address this challenge, mussel-inspired polydopamine (PDA) chemistry was exploited for surface engineering of the pore channels of PCTMs. It can be envisioned that the establishment of a PDA platform rich in catechol and amine groups on the pore surfaces would provide an ideal environment to accommodate metal ions, facilitating the heterogeneous nucleation and interfacial growth of MOF crystals. Meanwhile, the PDA interface would enhance the mechanical strength of the composite membrane as well as isolated 1D MOF superstructures.

To facilitate the effective modification of the inner surfaces of PCTM, the polymerization of dopamine was performed in a laboratory-made apparatus (Fig. 5) with the membrane suspended in the reaction solution. Strong shear force was provided by rigorous stirring to prevent the blocking of the pore entrances by some of large-sized PDA aggregates. Fig. 4a shows the section view SEM image of PDA modified PCTM with well-preserved pore arrays. The color change of the membrane from white to dark brown (Fig. 4a, inset) indicates the deposition of PDA. Conformal PDA nanotubes with a wall thickness of ca. 12 nm were obtained after template dissolution, suggesting the generation of uniform PDA layers on the inner surfaces of the pore arrays (Fig. 4b). Further evidence to support the successful formation of PDA layer was provided by ATR-FTIR analysis. The characteristic peak in the ATR-FTIR spectrum (Fig. 5a, blue) at 1601 cm\(^{-1}\) is assigned to the bending vibration of aromatic ring which is absent in the spectrum of pristine PC membrane (Fig. 5a, black). Additionally, the broad peak spanning 3600 cm\(^{-1}\) to 3000 cm\(^{-1}\) corresponds to the O-H and N-H stretching vibrations.

Then, ZIF-8 was employed as a prototype for fabricating 1D MOF superstructures from the PDA modified PCTM templates. After the contra-diffusion synthesis, the pore arrays of the membrane were maintained (Fig. 6a) with small-sized ZIF-8 nanoparticles homogeneously deposited on the inner surfaces (Fig. S8). Template removal resulted in well-defined 1D hollow ZIF-8 nanotubes replicating the dimension of the pore arrays (Fig. 6b). The nanotubes showed greatly improved structural regularity compared to those obtained from native PCTM templates. Uniform channels with an inner diameter of 150 nm could be observed. Particularly, massive production of the 1D ZIF-8 nanotubes with identical length (ca. 10 μm) equivalent to the thickness of the PCTM and an aspect ratio up to 40 was achieved (Fig. 6c). The inset shows the preserved pore entrance of ZIF-8 nanotubes. Energy-dispersive X-ray spectroscopic (EDX) mapping (Fig. 6d) and profile scanning (Fig. 6e) of the corresponding elements suggested that the structure of 1D ZIF-8 nanotubes was actually a hybrid with amorphous PDA interface, corresponding to a poor polycrystalline structure with
a relatively weak electron diffraction ring (Fig. 6b, inset). More evidence was provided by the ATR-FTIR and XRD analysis. After the contra-diffusion synthesis, the resulting composite membrane, labelled as PCTM@PDA@ZIF-8, exhibited characteristic bands in the spectral region of 1411 cm\textsuperscript{-1} and 1307 cm\textsuperscript{-1} assigned to the plane stretching and bending of imidazole ring, respectively (Fig. 5a, red). The absorbance at 3136 cm\textsuperscript{-1} and 2931 cm\textsuperscript{-1} was attributed to the aromatic and aliphatic C-H stretching vibrations of the 2-methylimidazole ligands.\textsuperscript{66} This proved the incorporation of the ZIF-8 crystals into the pore arrays of PCTM templates. Meanwhile, for the isolated 1D ZIF-8 nanotubes (PDA@ZIF-8), except the characteristic peaks of ZIF-8 crystals, absorption signals of PDA, such as the broad band over 3000 cm\textsuperscript{-1} (catechol hydroxyl) and the clearly resolved peak at 1617 cm\textsuperscript{-1} (aromatic ring), were observed in the FT-IR spectrum (Fig. 5b, red), indicative of the hybridized structure of the ZIF-8 nanotubes. Besides, XRD patterns of PCTM@PDA@ZIF-8 and the isolated hybrid ZIF-8 nanotubes showed a consistency with native ZIF-8 crystals (Fig. 7), which also confirmed the formation of ZIF-8 crystals within the pore channels of PCTM templates.

Specific surface area and porosity of the ZIF-8 nanotubes as well as the PCTM@PDA@ZIF-8 composite membranes were evaluated by nitrogen sorption-desorption measurements at 77 K. It can be seen in Fig. 8 that both native ZIF-8 crystals and the PDA hybridized nanotubes exhibit a type-I isotherm. The BET specific surface area was estimated to be 1303 m\textsuperscript{2}/g and 1014 m\textsuperscript{2}/g, respectively. The formation of PDA hybrid structure resulted in a decrease in the BET specific surface area, which might be attributed to the shielding effect of the compact PDA shell. This also resulted in a slight decrease in pore volumes from 0.71 cm\textsuperscript{3}/g of the native ZIF-8 to 0.65 cm\textsuperscript{3}/g of the hybrid ZIF-8 nanotubes. For the composite membranes, template synthesis of ZIF-8 nanotubes also introduced a large number of micropores exhibiting strong adsorption of nitrogen in the low pressure range. The BET specific surface area showed an evidence increase from 13 m\textsuperscript{2}/g to 99 m\textsuperscript{2}/g. Besides, preserved macropores were observed on both sides of the membranes after the contra-diffusion synthesis (Fig. S9). The porous properties of PCTM@PDA@ZIF-8 composite membranes containing both macropores and micropores, which can balances the flux and adsorption capacity, are expected to benefit the separation applications. Thermogravimetric analysis (TGA) was used to examine the thermal stability of ZIF-8@PDA nanotubes (Fig. S10). Only a weight loss of 5% was observed till 500 °C, corresponding to the removal of guest and unreacted molecules. The thermal stability of ZIF-8@PDA nanotubes was
further evaluated by heating at 250 °C under N₂ for 24 hours. After the heating treatment, the nanotubes presented no distinct change in crystal structure and morphology (Fig. S11), which confirmed the thermal stability of the nanotubes.

As demonstrated above, the introduction of PDA to the inner surfaces of the pore arrays of PCTM promoted the template synthesis of 1D ZIF-8 superstructures. Here, the PDA served as a coordination platform to accommodate the zinc ions, which facilitated the heterogeneous nucleation and growth of ZIF-8 crystals, as well as an interface-strengthening agent to improve the structural stability of the resulting 1D superstructures. First, by the existence of abundant catechol and amine species, PDA can effectively coordinate with transition metal ions, including Zn(II), via the formation of metal-catechol and/or metal-nitrogen-donor complexes. Up on contact with the imidazole ligands, the Zn(II) anchored sites acted as nucleation centers to induce the confined growth of ZIF-8 crystals on the PDA surface, preventing the formation of discrete ZIF-8 crystals in the solution to block the diffusion path of the imidazole ligands. Therefore, hollow ZIF-8 nanotubes with uniform channels spanning across the channels of the membrane were obtained. On the other hand, it has been reported that the metal-catechol coordination complexes may exhibit near-covalent stiffness and strength. This would stabilize the intergrown ZIF-8 crystals, resulting in well-defined 1D hybrid ZIF-8 nanotube after the dissolution of the PCTM templates.

The versatility of the PDA mediated template synthesis strategy was examined for preparing 1D superstructures for other kinds of MOFs. Following the established procedure, contra-diffusion synthesis of ZIF-67, ZIF-12, and HKUST-1 were performed. Due to the structural and composition similarity with ZIF-8, ZIF-67 exhibited a confined growth behavior along the pore walls of PCTM template (Fig. 9a). Self-supported 1D ZIF-67 nanotubes with uniform channels and a length equivalent to membrane thickness were obtained (Fig. 9b). But for ZIF-12, relatively large-sized particles were observed in the section view SEM image (Fig. 9c), and hollow 1D ZIF-12 superstructures with a reduced aspect ratio were finally obtained (Fig. 9d). ZIF-12 is composed of cobalt nodes coordinated with benzenimidazole (bIM) ligands. Since PDA could also provide strong binding to the cobalt ions, the limited length of the ZIF-12 superstructures might be attributed to the diffusion hindrance of the bIM ligands in the PDA modified pore channels. Unlike the mIM ligands, bIM is a heterocyclic aromatic compound with the fusion of benzene and imidazole units. Thus, the diffusion of bIM ligands would be hindered to some extent due to the strong interactions with the PDA layer, such as π-π stacking and hydrogen bonding, thereby resulting in a limited diffusion path and uncontinuous growth of ZIF-12 crystals in the pore channels. Interestingly, with the introduction of PDA, the HKUST-1 showed different growth behavior during the contra-diffusion synthesis, as compared to the situation within native PCTM templates. HKUST-1 particles with a decreased size (less than 260 nm) were formed in the pore channels (Fig. 9e). And, the confined growth of HKUST-1 crystals on the PDA surface generated 1D hollow superstructures with a length > 2 μm instead of short HKUST-1 nanorods (Fig. 9f). This demonstrated the benefits of PDA for the anchoring of MOFs on an inert surface. Nonetheless, due to relatively large crystal size of HKUST-1 as well as the diffusion...
limits of the aromatic BTC ligands, it remains challenging to prepare longer 1D hollow HKUST-1 nanotubes with ideal channels. The XRD and FTIR results of corresponding MOFs were listed from Fig. S12 to Fig. S17, confirming the formation of MOF crystals in the pores of template as well as the nanotubes.

Subsequently, we examined the potential application of the composite membrane for separation of methylene blue, a typical organic contaminant in wastewater. Taking advantage of the ZIF-8 functionalized composite membrane, effective separation of the organic dye was achieved using a simple filtration mode. Digital photo of the ZIF-8 composite membrane was previously shown in Fig. 6a (inset) with a functionalized area of 1.2 cm². Under a flow rate of 3 mL/min, the methylene blue in the solution was readily separated. The UV-vis spectra of the original methylene blue solution and the filtrates across the composite membrane were shown in Fig. 10. With the confined growth of ZIF-8 in the pore channels, the functionalized composite membrane showed a removal ratio of 92% for the methylene blue. The composite membrane can be functionalized and retained its morphology, with a filtration rate of 3 mL/min, and a removal ratio of 92% for the methylene blue. The composite membrane was tested for its effectiveness in removing methylene blue from aqueous solutions.

In summary, this study presents a facile and adaptable contra-diffusion synthesis of 1D MOF superstructures within the porous array of polycarbonate track-etched membranes (PCTMs) by tuning the surface chemistry. In a native PCTM template, the nucleation and growth of ZIF-8 could be promoted according to a catalytic transesterification mechanism to activate the specific imidazole ligands. Surface modification of the pore channels by the bio-inspired polydopamine (PDA) chemistry provided better controllability to regulate the template synthesis of MOFs. The PDA served as anchor bars of metal ions, facilitating the confined growth of MOF crystals with reduced size to form well-defined nanotubes with uniform channels, and also as interface-strengthening agent for the fabrication of robust 1D MOF superstructures after template removal. 1D hybrid ZIF-8 nanotubes spanning across the entire thickness of the template (10 µm) were obtained with an aspect ratio reaching up to 40. The versatility of the PDA mediated template synthesis strategy has been demonstrated in preparing 1D superstructures for other MOFs such as ZIF-67, ZIF-12, and HKUST-1 with different morphologies. The as-synthesized ZIF-8 integrated PCTM was proved to be able to effectively separate the organic dye in a filtration system. To conclude, this study provides new insight into the surface chemistry directed growth behavior of MOFs within confined channels of polymeric templates. Furthermore, the PDA mediated synthetic strategy is believed to bring about vast opportunities for template synthesis of more MOF superstructures for diverse applications.

Conflicts of interest

There are no conflicts to declare.

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Novel contra-diffusion synthesis of diverse 1D MOF superstructures in the channels of polycarbonate track-etched membranes regulated by a substrate-involved catalytic transesterification mechanism or mediated by the mussel-inspired polydopamine chemistry.