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Permselective 2D-polymer-based membrane tuneable by host–guest chemistry†

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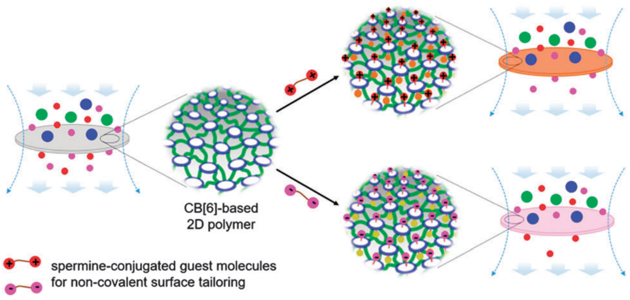
A permselective membrane with a non-covalently tailorable surface has been fabricated by deposition of a cucurbit[6]uril-based 2D polymer film onto a simple support membrane. Tuneable permselectivity of this membrane has been achieved through non-covalent surface modification using the remarkable host–guest chemistry of the incorporated cucurbit[6]uril units.

Over the decades, permselective nanoporous membranes have been widely used in various applications, including water purification,[1–3] gas separation,[4] the separation of biomacromolecules[5] and pharmaceuticals,[6] and sensing.[7] For many of these applications, the permselectivity is controlled by non-covalent interactions between the membrane and diffusing molecules; the membrane has to be carefully designed for each analyte.[8,9] However, the preparation of a bespoke nanoporous membrane for each purpose is not a trivial task and usually requires laborious, time-consuming, and multi-step processes.[10] Thus, the development of a simple nanoporous membrane that can be non-covalently functionalised to endow the desired permselectivity has been a long sought goal. Two-dimensional (2D) polymer films are promising candidates for permselective separation membranes,[11,12] because of their 2D meshwork structure and desirable mechanical properties. However, for 2D polymers to be functionalised non-covalently they must incorporate a molecular recognition element. We envisioned that a host–guest system incorporated into a 2D polymer could be a route to a membrane with tuneable permselectivity.

Cucurbit[*n*]urils (CB[*n*], $n = 5–8, 10, 14$) are a family of hollow pumpkin-shaped molecules with remarkable host–guest chemistry.[13–21] Recently, we reported the preparation of covalently self-assembled CB[6]-containing materials such as polymer nanocapsules[22–24,26] and 2D polymer films.[25,26] The incorporated CB[6] units in these materials are addressable by various guest molecules, such as the high affinity guest, spermine; therefore, we can modify the surface properties of these materials by simple treatment with spermine-conjugated molecules.[22–24,27]

Herein, we report a facile fabrication of a permselective membrane using a CB[6]-based 2D polymer film, and its tuneable separation properties (Scheme 1). The membrane can be easily prepared by simple filtration of a dispersion solution of the CB[6]-based 2D polymer film onto a commercially available supporting membrane. The 2D polymer-deposited membrane itself exhibited size-selective permeation, and the permselectivity was tuned by addition of spermine-conjugated guest molecules bearing charged or hydrophobic groups that modified the surface properties of the membrane.

To prepare the tuneable permselective membrane, 2D polymer was synthesized using previously reported procedures.[25] Briefly, the CB[6]-based 2D polymer film was prepared by photopolymerization of perallyloxyCB[6][28] and 1,2-ethanedithiol linkers (see ESI†). The resulting 2D polymer was deposited onto a polytetrafluoroethylene (PTFE) membrane in a commercially available syringe filter (~0.2 μm pore) for enhanced mechanical stability and ease of handling. This was achieved by gentle filtration of a dispersion solution of the 2D polymer through the membrane. Scanning electron microscopy (SEM) and Fourier



Scheme 1 Non-covalent surface tailoring of permselective membranes through host–guest chemistry of CB[6].

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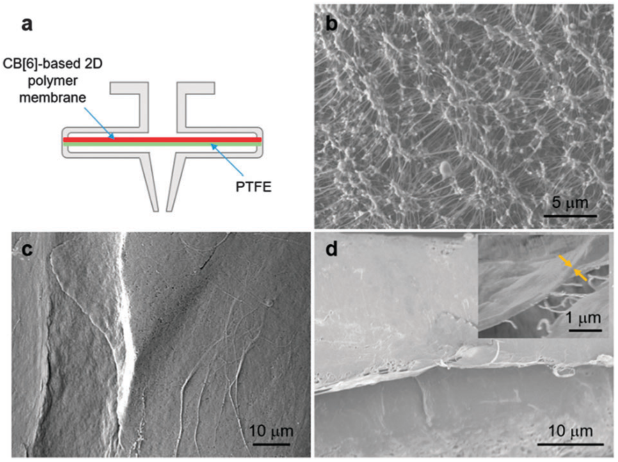

Fig. 1 (a) Schematic representation of the 2D polymer deposited permselective membrane in the syringe filter. SEM images of the surface of the bare PTFE membrane (b), and the CB[6]-based 2D polymer deposited PTFE membrane (c and d). Inset: The yellow arrows indicate the cross-section of the deposited 2D polymer film. The thickness of the deposited film is approximately 100 nm.

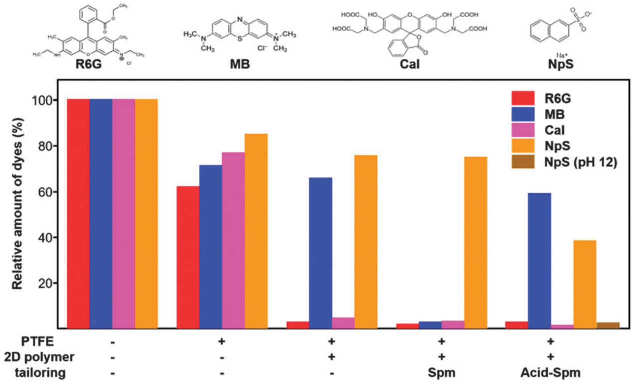

Fig. 2 Molecular separation performance of the CB[6]-based 2D polymer-deposited permselective membranes depending on the non-covalent surface tailoring with Spm and acid-Spm. Inset shows the structure of the dye molecules methylene blue (MB), rhodamine 6G (R6G), naphthalene sulfonate (NpS), and calcein (Cal).

transform infrared spectroscopy (FT-IR) revealed that the 2D polymer was evenly deposited on the surface of the supporting PTFE membrane, and the thickness of the deposited 2D polymer was approximately 100 nm (Fig. 1c, d and Fig. S1, ESI†). Nanoindentation measurements revealed the outstanding mechanical properties of the CB[6]-based 2D polymer: an elastic modulus of 25.3 ± 3.3 GPa and a hardness of 0.60 ± 0.11 GPa.[29] We note that our system is not a defect-free monolayer film. However, the simple fabrication procedure results in multilayer stacking of the 2D polymer, thereby compensating for any defects and preventing unwanted permeation through the membrane.

The permselectivity of the multilayer 2D polymer membrane was investigated using four common dyes that varied in size and charge. Aqueous solutions of the dyes, methylene blue (MB), rhodamine 6G (R6G), naphthalene sulfonate (NpS), and calcein (Cal), were each filtered through a membrane and dye content in the filtrate measured by fluorescence or ultraviolet-visible (UV-Vis) spectroscopy (Fig. 2 and Fig. S3, ESI†). Interestingly, most of the MB and NpS molecules passed through the 2D polymer membrane, the small losses were mainly due to the supporting PTFE membrane. In contrast, the R6G and Cal molecules were almost completely filtered off by an identical membrane, which may indicate that the 2D polymer-deposited membrane itself has a certain size selectivity that discriminates a naphthalene or anthracene-based dye from a fluorescein-based dye. In addition, after three filtration cycles, the size selectivity of the membrane was retained, suggesting that the mechanical stability of the permselective membrane is strong enough to be recycled presumably because of the heavily cross-linked network structure and the multilayer stacking of the 2D polymer (Fig. S4, ESI†).

The separation selectivity can be easily tuned by treating the membrane with spermine derivatives containing either positive (Spm) or negative charges (acid-Spm) through the strong host–guest interaction between CB[6] and spermine (Fig. 2). Once a stable host–guest complex between the CB[6] unit in the 2D polymer and Spm has formed, the surface of the 2D polymer membrane is cationic (see ESI†),[30] which dramatically reduced the permeation of the positively charged MB molecules probably because of Coulombic repulsion. Similarly, the acid-Spm-decorated 2D polymer membrane reduced the permeation of the negatively charged NpS molecules; however, a significant amount of NpS molecules passed through the membrane. We believe that this arose from a charge screening effect by the positive charge at the unmodified end of spermine threaded with the nearby CB unit. To enhance the anionic selectivity, the acid-Spm-modified membrane was treated with a pH 12.0 buffer solution, which may minimize the charge screening effect by neutralizing ammonium groups of spermine.[31] As a result, the negatively charged NpS molecules were efficiently retained on the membrane. These results show that the membrane-supported 2D polymer containing host CB[6] units can be tailored to give the desired permselectivity upon treatment with an appropriately functionalised guest molecule.

The hydrophobicity-dependent permeation was also demonstrated in a similar manner (Fig. 3). The CB[6]-based 2D polymer was deposited onto a commercially available porous anodic aluminum oxide (AAO) membrane with a one-dimensional channel with an average diameter of 200 nm (Fig. S1 and S2, ESI†). The membrane supported 2D polymer was treated with two different spermine derivatives: one contained triethylene glycol moiety (TEG-Spm, hydrophilic) and the other a dodecane moiety (C12-Spm, hydrophobic). The prepared membranes were each connected to the middle of a U-shaped tube with a cell at either side. The feed cell was filled with a 1.0 mM solution of $[Ru(bpy)_3]Cl_2$ (Rubpy) or rose bengal (RB) and permeate cell contained pure water (Fig. S5, ESI†).[32] These two molecules are similar in size but Rubpy is more hydrophobic.[32] The diffusion rates of Rubpy and RB through the membranes unmodified or modified with the spermine derivatives were examined by time-dependent UV-Vis absorbance changes in the permeate cell every 5 hours for 15 hours. The concentrations of the diffused

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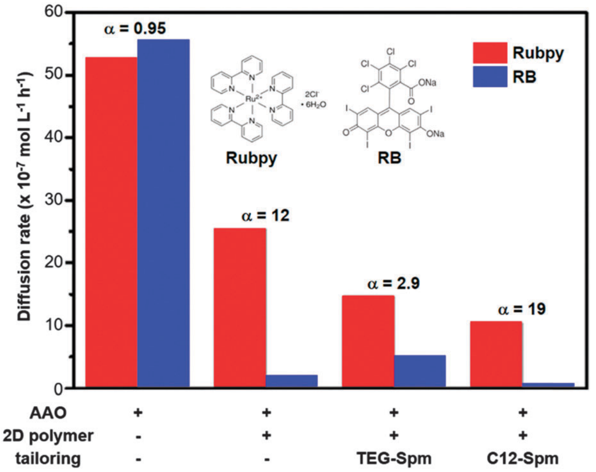

Fig. 3 Transport of Rubpy and RB through the permselective membranes with the unmodified 2D polymer and the modified 2D polymers with TEG-Spm and C12-Spm. The separation factor, α, was calculated by the ratio of diffusion rates of Rubpy and RB. Inset shows the structure of Rubpy and RB.

Rubpy and RB molecules in the permeate cell linearly increased as a function of time. Therefore, the separation factor can be calculated simply by the ratio of diffusion rates of Rubpy and RB. Without the deposition of the 2D polymer, the AAO membrane showed almost no selectivity for either dye; after deposition of the 2D polymer it selectively allowed permeation of the Rubpy molecules over the RB molecules by the factor of approximately 12. The separation factor further increased to 19 by the surface modification with the hydrophobic C12-Spm molecules, whereas it decreased down to 3 by the introduction of the hydrophilic TEG-Spm. These results show that the membrane-supported 2D polymer can be non-covalently tailored to give permselectivity on the basis of hydrophobicity, and its permselectivity is comparable or slightly better compared to earlier studies with other nanoporous materials.[32–35]

In summary, we have shown that the 2D polymer containing CB[6] molecules is able to form a permselective membrane. Furthermore, we have shown that by non-covalent surface modification the permselectivity of the polymer can be tuned. We have demonstrated the selective permeation with common dye molecules; however, we believe that by careful choice of guest molecule this approach will be applicable to more important analytes. Therefore, we anticipate that this CB[6]-based 2D polymer membrane will provide an opportunity for future developments in membrane separation technologies because of the easy fabrication process, and the facile tuning of separation properties through host–guest chemistry.

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