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Homeotropic Alignment and Selective Adsorption of Nanoporous Polymer Film Polymerized from Hydrogen-bonded Liquid Crystal

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Electronic Supplementary Information

Abstract Nanoporous polymer film with a hexagonal columnar (Col_h) structure was fabricated by templated hydrogen-bonding discotic liquid crystals containing methacrylate functional group. The supramolecular hydrogen-bonded complex T3Ph-L is composed of a 1,3,5-tris(1*H*-benzo[d]imidazol-2-yl)benzene (T3Ph) core molecule as the hydrogen-bonding acceptor and 3,4,5-tris((11-(methacryloyloxy)undecyl)oxy)benzoic acid (L) peripheral molecules as donors. And the Col_h structure is always retained after self-assembly, photo-crosslinking, and removal of the template T3Ph. The nanoporous polymer film can retain the Col_h phase even under the dry condition, which indicates more possibilities for practical applications. After chemical modification of the inner wall of the nanopores, the nanoporous polymer film with pores of about 1 nm selectively adsorbs ionic dyes, and the adsorption process is spontaneous and exothermic in nature. Homeotropic alignment can be obtained when the blend complex was sandwiched between two modified glasses after annealing by slow cooling, which shows that the nanoporous polymer film has potential in applications such as nanofiltration.

Keywords Liquid crystal; Hydrogen bonding; Homeotropic alignment; Nanoporous polymer film; Selective adsorption

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INTRODUCTION

Nanoporous films have been explored for many years because of their broad application prospects.^[1,2] Their excellent mechanical properties, easy processability, large specific surface areas, and well-defined porosity are desirable for practical applications.^[3] Many efforts have been made on utilizing self-assembled block polymers (BCPs) to create aligned nanoporous morphology.^[4–7] Nevertheless, the pore size is difficult to be controlled to be lower than 10 nm in this approach, which has limited the applications of BCP-based nanoporous polymer films, such as nanofiltration.^[8–11] Another approach involving the self-assembly and crosslinking of hydrogen-bonded discotic liquid crystals followed by removing the template has the advantages of intrinsically small size (with periodic sizes of a few nm) and inherent exact size distribution, which are crucial in nanofiltration.^[12–15] Up to now, most research works in this end have resulted in non-aligned nanoporous polymer films.^[16–18] Unfortunately, the performance of nanoporous polymer films is restricted by the non-aligned nanostructured morphologies.^[19,20] Nanopores with the wrong orientation will not be

useful for filtration. In nanofiltration membranes, the unimpeded nanopores will ensure filtration efficiency. In order to encourage a broader range of applications, nanoporous polymer films with a homeotropic alignment of columnar mesophases over large areas are of great significance.

Liquid crystals usually prefer planar alignment by common processing methods such as shearing the samples in columnar mesophases. Homeotropic alignment has been explored by the use of external fields, such as magnetic^[21–23] and electric fields^[24,25] and polarized light.^[26] However, these methods are inconvenient to operate and utilize on a large scale. Another method has been explored, which involves tuning the interfacial energy to match the discotic liquid crystals by chemical modification and thermal annealing under confinement of two solid surfaces.^[27–29] According to the principle of homeotropic alignment,^[30] it is necessary to increase the surface polarity when there is strong hydrogen bonding in the system. Some reports have shown that discotic liquid crystals have the potential for homeotropic alignment.^[30,31] Unfortunately, with increasing degree of crosslinking or under dry conditions, the structures in nanoporous films may be destroyed.

In this work, a supramolecular hydrogen-bonded complex T3Ph-L is composed of one 1,3,5-tris(1*H*-benzo[d]imidazol-2-yl)benzene (T3Ph) core molecule as the hydrogen-bonding acceptor and three 3,4,5-tris((11-(methacryloyloxy)undecyl)

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oxy)benzoic acid (L) peripheral molecules as donors, as shown in Fig. 1. The template core molecule T3Ph can form columnar liquid crystalline (LC) phases with a series of benzoic acid derivatives according to the literature.^[32] And the design of the donor molecule L was based on how to co-assemble with T3Ph to obtain a hexagonal columnar (Col_h) structure and fix the phase structure of the complex efficiently.^[33,34] Acrylate functional group was considered first to be incorporated as substituents on the phenyl ring of L for locking the desired Col_h structure. With the consideration of the chemical stability during the synthesis and storage of L,^[35] methacrylate tails were chosen instead. The additional methyl group made the molecule less prone to hydrolysis and Michael addition reactions. Homeotropic alignment was realized after annealing the complex between two surface-modified glasses. After crosslinking and chemical modification of the inner wall of the nanopores, the nanoporous polymer film selectively adsorbed ionic dyes with charges different from those on the inner wall, and the adsorption process was found to be spontaneous and exothermic in nature.

EXPERIMENTAL

Materials

Divinylbenzene (DVB) was purified by column chromatography (silica gel) to remove polymerization inhibitor before use. T3Ph was synthesized according to the literature.^[32] The product was purified by recrystallization and sublimation before use. L was synthesized according to the synthetic route as shown in Scheme S1 (in the electronic supplementary information, ESI). And the chemical structures of T3Ph, L, and DVB in the hydrogen-bonded complex are shown in Chart S1 (in ESI).

Preparation of the Hydrogen-bonded Complexes

Required amounts of T3Ph and L with a molar ratio of 1:3 were dissolved in chloroform. Then a few drops of methanol were added to the mixture solution to assist dissolution of T3Ph. The solvent was slowly evaporated at ambient temperature, and the supramolecular complexes T3Ph-L were dried in vacuum for 24 h. Homogeneous samples were prepared by addition of a certain amount of the crosslinker DVB to the hydrogen-bonded complexes and triple centrifugation with 1.0×10^4 r/min for 10 min to ensure homogeneous mixing.

Thermal Annealing and Homeotropic Alignment of the Supramolecular Complex

First, the glass slides were pretreated by a piranha solution at 90 °C for 30 min, cleaned by Milli-Q water and ethanol, and dried by N₂. The surfaces of the cleaned glass slides were modified by spin-coating a 10 wt% aqueous solution of poly(sodium 4-styrenesulfonate) (PSS) with a spin speed of 1500 r/min for 60 s. The supramolecular complex containing 30 wt% of DVB was sandwiched between two surface-modified glass slides and the thickness was controlled by the amount of sandwiched blends. The samples were thermally annealed by heating to the isotropic state and then cooled down slowly (0.1 °C/min) to ambient temperature.

Photo-crosslinking of the Supramolecular Complex

The supramolecular complex containing 1 wt% radical photo-initiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide was polymerized by exposure to a 365 nm UV light chamber (160 W) for 1 h followed by a benchtop lamp (16 W) for 48 h.

Preparation of the Nanoporous Polymer Film

The polymerized samples were separated from the substrate after water immersion and then immersed in dimethylsulfoxide (DMSO) at ambient temperature for 48 h. And then the samples were washed with Milli-Q water to eliminate any residual DMSO.

Selective Adsorption of Ionic Dyes

The nanoporous polymer film with thickness near 60 μm was cut into small pieces and immersed in 0.1 mol/L KOH solution to deprotonate the carboxylic acid moieties. And the samples were washed with Milli-Q water to remove any residual base. Methylene blue (MB) and methyl orange (MO) dyes were dissolved at a certain concentration in Milli-Q water to ensure relative absorbance of approximately 1 (MB + MO). The modified nanoporous polymers were immersed in an aqueous solution of MB and MO to adsorb the dye molecules at ambient temperature overnight. The adsorption was monitored by UV-Vis spectroscopy.

Adsorption of MB at Different Temperatures

A series of aqueous solutions of MB with different weight fractions ($c = 40 \times 10^{-7}$, 60×10^{-7} , 80×10^{-7} , 100×10^{-7} , and 120×10^{-7}) were prepared. To evaluate the thermodynamic properties, 10 g of prepared aqueous solution of MB with 2 mg of nanoporous polymer film was placed at 20 or 40 °C until equilibrium was reached. The adsorption was monitored by UV-

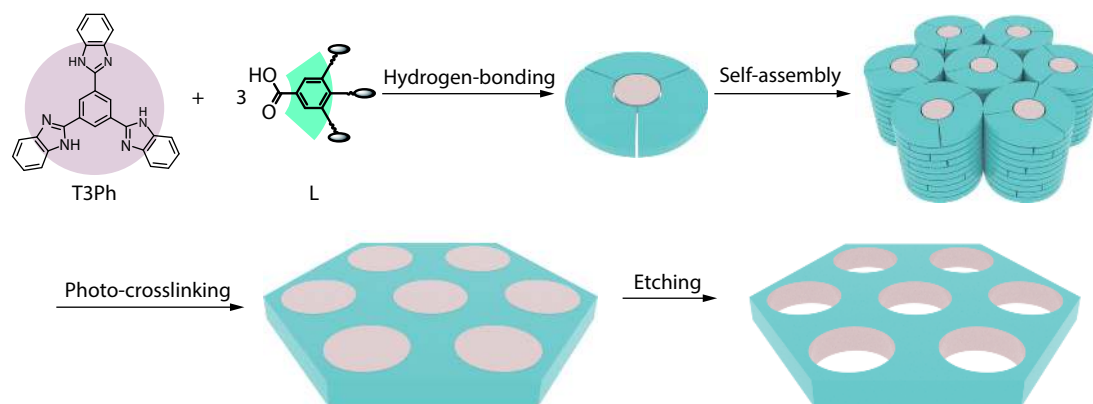


Fig. 1 Schematic illustration for the preparation of the nanoporous polymer.

Vis spectroscopy.

RESULTS AND DISCUSSION

Preparation and Characterization of the Hydrogen-bonded Complexes

The hydrogen-bonded complex T3Ph-L was prepared by mixing the solution of T3Ph and L in a 1:3 molar ratio followed by slow evaporation of the solvent at ambient temperature. The thermotropic LC behavior of the complex was examined by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and polarized light microscopy (PLM). Fig. S2(a) (in ESI) shows a series of first-cooling and second-heating DSC thermograms of molecule T3Ph, L, and the complex T3Ph-L at a rate of 10 °C/min under nitrogen atmosphere after elimination of thermal history. The DSC curves of the complex T3Ph-L show no phase transitions of the individual components, which indicates that the L molecules are fully complexed to T3Ph by intermolecular hydrogen bonds. The DSC results only show the crystal-to-LC phase transition, and the isotropization of the LC phase is not observed. Therefore, the isotropization temperature (190 °C) was only determined by PLM. According to the literature,^[35] systems containing the methacrylate functional group could not be heated over 100 °C to prevent thermo-crosslinking. Thus, we attempted to decrease the isotropization temperature of the system by doping a small molecule. DVB^[31] is a common liquid crosslinker, and it should have little influence on the phase structure of the complex because of its nonpolar property. The DSC results (Fig. S2b in ESI) show no additional phase transitions after DVB was doped into the complex. On the basis of PLM results (Fig. S3a in ESI), the isotropization temperature gradually decreases with increasing content of DVB. It decreases to be lower than 100 °C when the blend sample contains 30 wt% of DVB. And the Col_h mesophase is still formed with the addition of a small quantity of DVB. When the content of DVB in the blend increases, the *d*-spacing (*d*₁₀₀) of the Col_h phase increases (Fig. S3b in ESI). DVB is miscible with L and immiscible with T3Ph. We propose that DVB swells the L molecule surrounding the core T3Ph and increases the periodic size of the mesophase.

Considering the above experimental results, we systematically characterized the complex T3Ph-L containing 30 wt% of DVB. The sample showed fan-shaped optical textures of columnar mesophases as observed by PLM (Fig. 2a). The WAXS profile of the blend sample containing 30 wt% of DVB (Fig. 2b) shows that three diffraction peaks in the low-angle region with a scattering vector ratio of 1:√3:2 could be assigned to the (100), (110), and (200) reflections of a Col_h phase. The intercolumnar distance *a* is calculated by $a = 2d_{110} = 4.1$ nm. And the distance between discs along the columnar axis *c* = 0.39 nm is calculated on the basis of the high-angle diffraction peak.

The formation of intermolecular hydrogen bonds in the complex was studied by FTIR (Fig. 2c). Compared with the individual components, the FTIR spectrum of the T3Ph-L complex shows that the C=O stretching vibration of benzoic acid shifts from 1716 cm⁻¹ to 1724 cm⁻¹ and an N-H stretching vibration at 3247 cm⁻¹ appears. These changes confirm the formation of intermolecular hydrogen bonds in the complex.

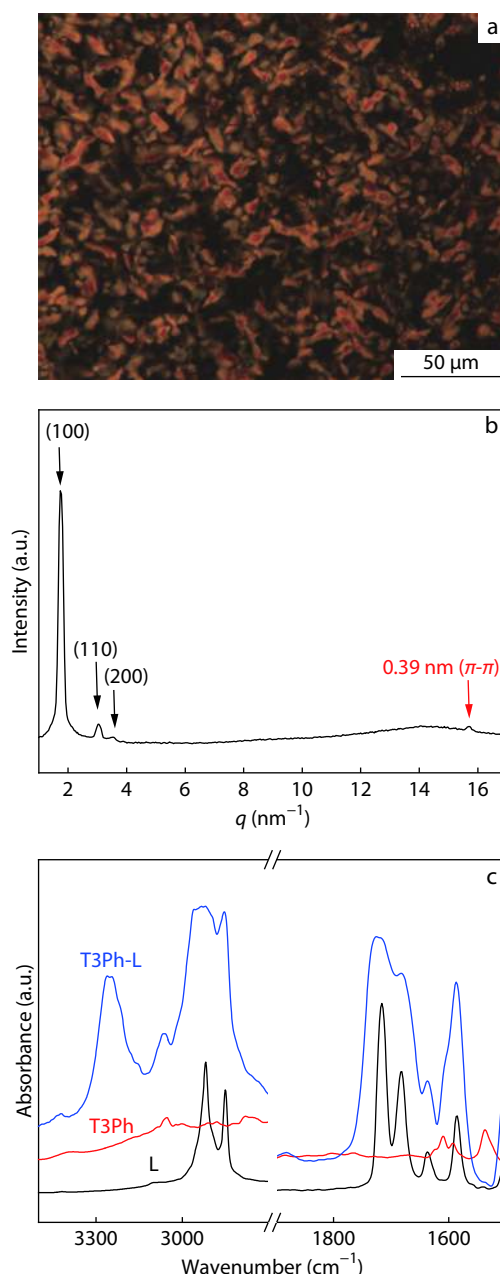


Fig. 2 PLM micrograph (a), WAXS profile (b), and FTIR spectra (c) of the complex T3Ph-L containing 30 wt% of DVB at ambient temperature.

Photo-crosslinking of the Supramolecular Complex

Photo-crosslinking by photoinitiated free-radical polymerization is an effective method for locking the structure of polymerizable LC assemblies. The methacrylate functional groups on the L molecule can effectively react with neighboring groups under UV irradiation with the presence of a photoinitiator, leading to a crosslinked polymer material. To examine the process of photo-crosslinking, the crosslinked polymer films were studied by FTIR (Fig. 3a). The intensity of the characteristic =C-H bending vibration band at 900 cm⁻¹ greatly reduces and the characteristic C=O stretching vibration band shifts from 1724 cm⁻¹ to 1720 cm⁻¹, clearly indicating that crosslinking occurs to produce

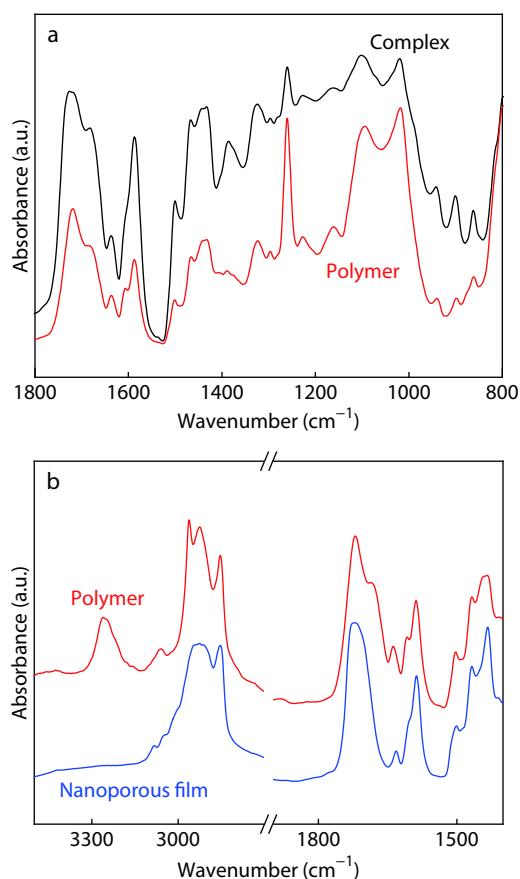


Fig. 3 FTIR spectra before and after polymerization (a) and those of the polymer before and after template removal (b).

a crosslinked polymer film.

The low-angle diffractions in the middle-angle X-ray scattering (MAXS) profile of the crosslinked polymer film (Fig. 4a) show a characteristic scattering vector ratio of 1:√3:2, indicating the retention of the Col_h mesophase after photo-cross-linking. In comparison with the sample before photo-cross-linking, the q_{100} value decreases 0.04 nm⁻¹, and the inter-

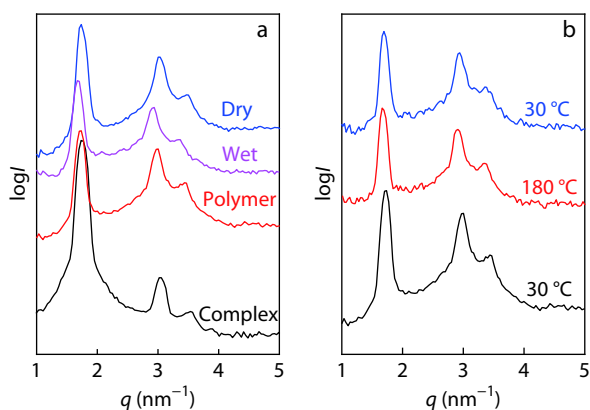


Fig. 4 MAXS profiles of the complex, the polymer after polymerization of the complex, the wet nanoporous polymer films after template removal, and the dry nanoporous polymer films (a) and those of the polymer film at different temperatures after polymerization (bottom curve: before heating; top curve: after cooling) (b).

columnar distance a increases 0.08 nm accordingly. And the thermal stability of the crosslinked polymer film was confirmed by MAXS (Fig. 4b). The MAXS results show that the Col_h phase of the crosslinked polymer film is stable upon heating, suggesting that a well crosslinked polymer network is produced after polymerization.

Homeotropic Alignment of the Supramolecular Complexes

Discotic liquid crystals may take homeotropic or planar alignment depending on the surface chemistry of the modified substrate. Homeotropic alignment can be obtained when the modified surfaces have a distinct affinity for the discotic core rather than the discotic periphery.^[30] The supramolecular hydrogen-bonded complex T3Ph-L contains a rigid core with strong polarity owing to the acid-base proton sharing and a non-polar periphery attributed to the alkyl chains of L. We speculate that a surface with strong polarity would have a strong affinity for the cores to realize homeotropic alignment. Inspired by the work of Osuji's group,^[31] we utilized PSS to tune the surface energy of the substrate to obtain homeotropically aligned films. At the same time, PSS as a sacrificial polymer layer is soluble in water, and thus the films are easier to be separated from the substrate.

We modified the glass surface by spin-coating a layer of PSS. When a certain amount of the complex having 30 wt% of DVB was sandwiched between two modified glasses and annealed by slow cooling (0.1 °C/min) from the isotropic state, homeotropic alignment was obtained, which supports the proposed preferential wetting mechanism.^[30,36,37] The extent of alignment was characterized by PLM, two-dimensional (2D) MAXS, and transmission electron microscopy (TEM). Under cross-polarizers, the complex exhibits the optical texture of a columnar mesophase after it was cooled down from the isotropic state. And under such conditions, homeotropic domains should appear black. During cooling at a rate of 0.1 °C/min, the area of black regions increases with decreasing film thickness (Fig. 5a). Under one polarizer, the growth of dendritic morphologies where the domains nucleate is observed (Fig. 5b). The 2D MAXS pattern (Fig. 5c) exhibits a 6-fold symmetry (hexagonal packing). Because DVB was also stained with RuO₄, the contrast of the sample under TEM observation is poor, and it was difficult to observe a clear pattern. However, a clear hexagonal pattern can be seen by means of filtered inverse-fast Fourier transformation (FFT). And the filtered inverse-FFT TEM micrograph of planar cut of the homeotropically aligned polymer film (Fig. S4 in ESI) shows the hexagonal domain in the micrometer scale.

Preparation of Nanoporous Polymer Films

Nanoporous polymer films were prepared by removing the template T3Ph from the crosslinked thin films with DMSO which is a good solvent for T3Ph. The removal of the template was confirmed by FTIR results. The FTIR spectrum (Fig. 3b) of the sample after removal of the template shows the disappearance of the N—H stretch vibration at 3261 cm⁻¹, in comparison with that of the crosslinked sample. After removal of the template, the phase structure is retained as confirmed by the MAXS profile (Fig. 4a) showing diffractions with a characteristic scattering vector ratio of 1:√3:2. Compared with the profile of the sample before removal of the template, the q_{100} value decreases

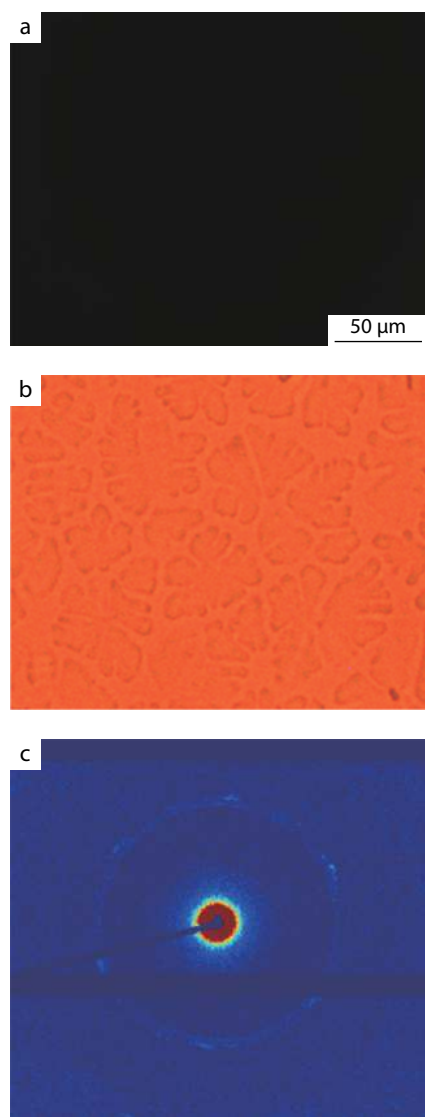


Fig. 5 PLM micrograph with cross-polarizers (a) and optical micrograph with one polarizer (b) of the complex containing 30 wt% of DVB at ambient temperature during cooling at a rate of 0.1 °C/min, and 2D MAXS pattern of the homeotropically aligned polymer film (c).

0.03 nm^{-1} , and the intercolumnar distance a increases 0.09 nm accordingly. When the nanoporous polymer films are washed by ethanol and dried at ambient temperature, the phase structure is also retained and the q_{100} value further increases 0.03 nm^{-1} , corresponding to a 0.09 nm decrease in the intercolumnar distance a . Therefore, the nanoporous polymer films retain the phase structure whether they are wet or dry.

The progress of removal of the template T3Ph was monitored by UV-Vis spectra (Fig. S5 in ESI). We immersed 2.2 mg of a crosslinked film without homeotropic alignment into 100 g of DMSO and measured the time-dependent UV-Vis adsorption of the solution at 316 nm. From the UV-Vis result of the T3Ph/DMSO solution, we estimate that T3Ph is removed from the crosslinked film after immersion for 24 h.

Adsorption of Ionic Dyes

After removal of the template T3Ph, $-\text{COOH}$ functional groups

are exposed on the inner walls of the nanopores, which is convenient for further chemical treatment and applications. The selectivity of the nanopores is determined by both the pore size and the charges on the pore surface. In this work, we focused on changing the charges of the pores by chemical treatment to realize selective adsorption. When the nanoporous polymer film is treated with an aqueous solution of potassium hydroxide, the pores will carry negative charges. Positively charged MB and negatively charged MO having approximately the same sizes (Fig. S6b in ESI) were chosen for adsorption experiments. The UV-Vis spectra show that MB has a strong absorption band at 664 nm and MO has a strong absorption band at 465 nm. A competitive adsorption experiment between MB and MO shows the evident decrease of the MB absorption band but almost no change of the MO absorption band after adsorption, which indicates that the nanoporous polymer film with negatively charged pores selectively adsorbs MB carrying positive charges (Fig. 6a).

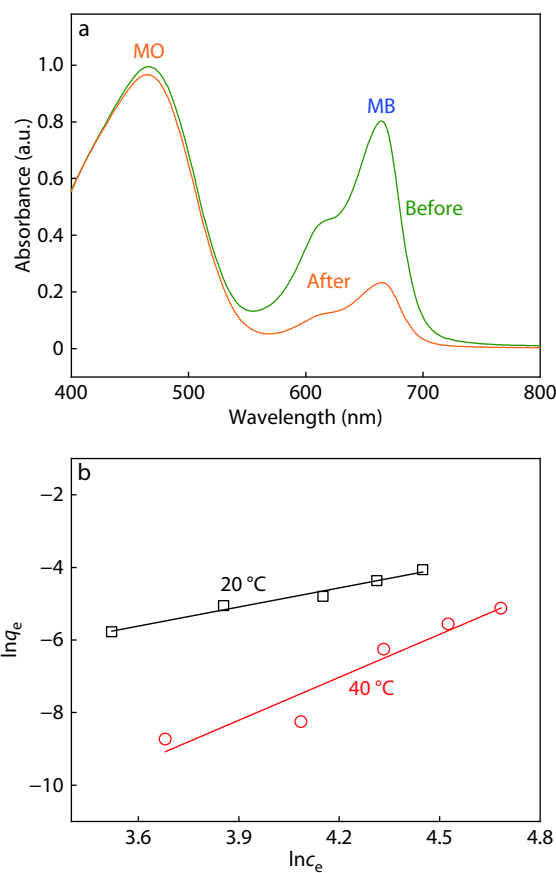


Fig. 6 UV-Vis spectra of the aqueous solution of MB and MO before and after adsorption (a) and Freundlich model of adsorption isotherms for MB (b).

The process of adsorption is determined by several factors, such as adsorbent dosage, contact time, and temperature.^[38,39] Temperature is one of the most important factors to influence the result of adsorption. To determine the effect of temperature, adsorption experiments were carried out at 20 and 40 °C. The adsorption capacity increases with decrease in temperature. When the initial weight fraction of

the solution is 120×10^{-7} , the maximum adsorption capacity decreases from 17.2 mg/g to 5.95 mg/g with the increase in temperature from 20 °C to 40 °C (Fig. S8b in ESI). This suggests that the adsorption process of MB onto the nanoporous polymer film is exothermic. In order to understand the adsorption mechanism, equilibrium adsorption isotherms are needed. The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface in solution. A straight line is fitted when $\ln q_e$ is plotted against $\ln C_e$. And Freundlich constant n and k_F can be obtained from the slopes and the intercepts in Eq. S(2) (Fig. 6b). The fitted values of n and k_F are 0.57 and 65.7×10^{-7} g/g, respectively, at 20 °C for the nanoporous polymer film. The Freundlich equation can be used to roughly evaluate the experimental results with a correlation coefficient R^2 (0.976 for 20 °C and 0.922 for 40 °C). And the fitted values indicate that MB can be absorbed easily by the nanoporous polymer film. The equilibrium adsorption isotherms are crucial for the potential applications of the nanoporous polymer film, which show that the adsorption process is spontaneous and exothermic in nature.

CONCLUSIONS

We prepared a nanoporous polymer film with a Col_h mesophase and homeotropic alignment. The Col_h mesophase of the nanoporous polymer film can be retained even under dry conditions. And the preparation of such films is a facile process because of the use of hydrogen bonding and PSS as a sacrificial polymer layer. The structural stability and facile preparation of the nanoporous polymer film indicate more possibilities for practical applications. The nanopores of the polymer film show a spontaneous and exothermic adsorption toward dyes with specific charges and certain sizes, which indicates broad application potential.

Homeotropic alignment is of crucial importance for practical applications of nanoporous polymer films with one-dimensional channels. And the principle of tuning the interfacial energy can be generally applied in the preparation of the nanoporous polymer film with decreasing film thickness. In practical applications, such as chemical separation membrane, nanoporous polymer films with no defects and sub-micron thickness are preferred to guarantee high selectivity and high flux at the same time. Further work aiming to prepare defect-free submicron-thick nanofiltration membranes is in progress.^[40,41]

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2431-9>.

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