

Nanoporous Supramolecular Liquid Crystal Polymeric Material for Specific and Selective Uptake of Melamine

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promising and prevalent perspective in selective adsorption, water desalination, ion conductivity, and so on. However, the specific recognition and selective uptake of some highly self-complementary hydrogen-bonded heterocyclic compounds (e.g., melamine) are extremely difficult for the widely used carboxylic acid-type discotic liquid crystals to competitively bind and remain challenging. Here, we report a nanoporous supramolecular liquid crystal polymeric material built on a photo-cross-linked melamine/ thymine-derivative supramolecular structure, which can specifically recognize and selectively absorb melamine from solutions. The



small pore diameter, specific hydrogen-bonded sites, and strong systematic binding in the hexagonal columnar nanochannels of the supramolecular polymeric material endow itself with a series of superior properties, including highly competitive uptake of melamine, stable adsorption even in harsh environments, and good adsorption recyclability. Moreover, the melamine adsorption capacity and kinetics of the supramolecular material are also investigated, which determines that the adsorption kinetics of the nanoporous liquid crystal polymeric material follow the Lagergren pseudo-second-order kinetic model.

INTRODUCTION

Nanoporous polymeric materials, with remarkable developments and applications in gas and solid separation, photoelectrochemistry, catalysis, and ion conductivity, relying on their superb mechanical, electrical, and chemical properties at nanoscales, have received extensive attention from the porous material research community.^{1–7} As the classical nanochannel materials, nanoporous polymeric materials although have been comprehensively investigated, their wide diameter distributions, modest porous homogeneities, free defects, and poor alignments resulted in unsatisfactory pore selectivity, which became a huge obstacle to the further development.^{8–11} Moreover, the broad distribution of pore sizes and highly tortuous nanochannels also limited the permeability and selectivity of ultrafiltration, leading to a low flux and decreased kinetics of filtrate in separation.^{11–14}

Thus, the accuracy control of monodisperse pore size and regulation of uniaxial orientation are two critical challenges in the development and application of nanoporous polymeric materials, which remind us of the nanoporous polymers built on cross-linked supramolecular discotic liquid crystals (LCs). On the one hand, supramolecular LCs can self-assemble through the noncovalent binding of the heterocyclic molecule cores, capable of narrowing the pores to the sub-1 nm and controlling the distribution of pore diameters;^{7,15–18} on the other hand, LC properties in combination with the fluidity of liquids and the anisotropic order of crystals can be utilized to

develop the orientational order over large areas.^{19–22} Meanwhile, the well-aligned morphologies can be fixed and retained by polymerization.^{23–31} After the removal of core templates, the self-assembled polymers can be transformed to the monodisperse nanoporous materials, which have exhibited advantageous prospects for molecular sieving and separation of toxic and hazardous substances.^{38,9,32–34}

Melamine, a common chemical raw material, has however attracted extensive concerns for pet foods contaminated with melamine and milk powder incidents.^{35,36} Many toxic effects from melamine, including kidney stones, bladder cancers, and clinical pathological changes, have been reported.^{35,36} It was undoubted that melamine as an environmental contaminant had a significant and sustained impact on food safety and renal function, which drove the exploration of the effective recognition and elimination of melamine. A great deal of research about melamine was focused on the melamine detection, since the protein determination method (the Kjeldahl method³⁷) was exploited to measure a falsely high

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Figure 1. Schematic illustration of the design and fabrication of supramolecular discotic liquid crystal polymeric material for specific and selective uptake of melamine.

Scheme 1. Synthetic Route of the Thymine-Functionalized T-Monomer with Three Long Aliphatic Alkyl Tails Bearing Terminal Acrylate Groups



protein concentration through the illegal addition of melamine,^{38,39} whereas the separation methods of melamine have been barely studied. The current known extraction techniques including solid phase extraction (SPE) and molecular imprinted polymers (MIPs) are restricted by the poor selectivity and complex time-consuming process of SPE and low rebinding capacity in MIPs, respectively.^{40–42}

Confronting this challenge, nanoporous supramolecular liquid crystal polymeric (LCP) material, with high selectivity, simple construction, and strong binding capability, stands out as an optimal choice for melamine elimination.^{15–17} Up to now, most of the known nanopore designs of self-assembled LCs relied on carboxyl or carboxylate groups of benzoic acid derivatives and fatty acids at the pore surfaces.^{7,10,15–19,22,30,32,33,43–50} Despite carboxylic acid derivatives

(e.g., 3,4,5-trialkoxybenzoic acid) when met with plenty of heterocyclic molecules being able to self-assemble into stable supramolecular discotic LC structures by the hydrogenbonding effect, they were hardly miscible and hydrogenbonded with pure melamine (not functionalized melamine derivatives) because the strong self-complementary hydrogenbonded matrix of melamine, which contributed to its extremely stable state and poor solubility, could not be destructed by carboxylic acids. Alternatively, a variety of complementary compounds have been previously screened to construct melamine-core hydrogen-bonded supramolecular LC complexes, which determined that the imidodicarbonyl unit of thymine was the best functionality and liquid crystallinity could be formed through melamine/thymine-derivative supramolecular complex.²¹ However, such an effective complementary

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Figure 2. (a) FT-IR spectra of melamine (top), melamine-core supramolecular complex (middle), and T-monomer (bottom). (b) ¹H NMR spectra of melamine-core supramolecular complex (top) and T-monomer (bottom).

imidodicarbonyl functionality, capable of breaking some highly self-complementary hydrogen-bonded units (e.g., melamine), has never been reported as the hydrogen-bond recognition site of any nanoporous supramolecular LCP material.

Inspired by all the above works, we report in this article a nanoporous polymeric material built on melamine/thyminederivative supramolecular discotic LC complex, which is utilized in two aspects: (1) selective recognition and separation of melamine; (2) strong binding and uptake of melamine even in harsh environments. As schematically illustrated in Figure 1, the nanoporous polymeric material is fabricated by photopolymerization/cross-linking of discotic LC molecules, each of which is constructed by a hydrogen-bonded supramolecular complex structure containing one melamine core and three thymine derivative compounds with three long aliphatic alkyl tails bearing terminal acrylate groups. After the removal of melamine cores via destruction of the internal hydrogen bonds, hexagonal columnar (Col_h) nanochannels are built in the corresponding polymeric material, which can be used to capture melamine in a synergistic, symmetrical, and complementary hydrogen-bonded combination mode for the specific uptake of melamine due to the size, charge, and spatial match selectivity. Moreover, the interactions of multiple hydrogen bonds build the strongly systematic binding to melamine, which promotes the recognition and adsorption of melamine even in harsh environments.

RESULTS AND DISCUSSION

Design and Synthesis of the Complementary T-Monomer and Melamine-Core Complex Monomer. The synthetic route of the complementary thymine-functionalized T-monomer with three acrylate groups is presented in Scheme 1, and the synthetic details are depicted in the Supporting Information. Methyl gallate (1) was engaged in a substitution reaction with 11-bromo-1-undecanol to yield compound 2. TBS protection of the hydroxyl groups of compound 2 afforded compound 3. The ester group of compound 3 was then reduced to a hydroxyl group to give compound 4. Thymine, an optimal complementary imidodicarbonyl derivative, was protected by tert-butyl carbonate (Boc) group to give a di-Boc compound 5, which was directly treated by a selective Boc deprotection approach (NaHCO₃) to provide the mono-Boc-protected compound 6. The Mitsunobu reaction linking compound 4 and thymine derivative 6 afforded compound 7 possessing three long TBS-protected alkyl tails, which were of crucial importance to the generation of liquid crystallinity. Compound 8 was synthesized through a desilylation reaction. Esterification of compound 8 with acrylyl chloride yielded compound 9. The desired polymerizable T-monomer with an imidodicarbonyl unit was successfully obtained through a trifluoroacetic acid treatment.

The melamine-core supramolecular complex was formed from a mixture containing T-monomer and melamine with a molar ratio of 3:1 as illustrated in Figure 1 and Scheme S2; the detailed complex formation procedure is described in the Supporting Information. Because of the strong hydrogenbonding interactions between the O=C-N-H units of the imidodicarbonyl groups of T-monomer and the H-N-C-N units of melamine, the resulting supramolecular complex appeared as a white waxy compound after solidification, which was often observed in room-temperature LC samples.

The formation of intermolecular hydrogen bonds was characterized by Fourier transform infrared (FT-IR) spectroscopy and ¹H nuclear magnetic resonance (¹H NMR) spectroscopy. As shown in Figure 2a, the -NH₂ stretching vibrational band of melamine, in comparison with that of melamine-core supramolecular complex, shifted from 3471 to 3421 cm⁻¹. The apparent red-shift confirmed the formation of hydrogen bonds between N-H (H_a) protons of melamine and C=O group of the imidodicarbonyl functionality. Furthermore, the significant signal at 1551 cm^{-1} in the supramolecular complex sample corresponded to the -C=N stretching vibration of the triazine ring, indicating that melamine did self-assemble with T-monomer to form a hydrogen-bonded complex monomer.

¹H NMR spectra of T-monomer and the corresponding melamine-core complex were measured in CDCl₃. As can be seen in Figure 2b, the chemical shift of N–H proton (H_b) of the imidodicarbonyl group in T-monomer shifted downfield from 8.03 to 8.74 ppm. The large downfield shift implied that the secondary amine of T-monomer was markedly influenced by hydrogen-bonding interactions between the hydrogen protons (H_b) of imide group and nitrogen atoms of the triazine ring. In addition, without the addition of other species besides T-monomer and melamine, a new peak at 6.20 ppm in the ¹H NMR spectrum of supramolecular complex represented the N-H proton (H_a) of melamine. Because of the poor solubility of melamine in CDCl₃, ¹H NMR usually showed no signal of free melamine. But if melamine could form hydrogen bonds with some complementary compounds, the proton signal of melamine in CDCl₃ could appear.⁵¹ Furthermore, if the integration of the proton $(H_{\rm h})$ of T-monomer was set as 1,



Figure 3. (a) POM image, (b) DSC thermogram, and (c) SAXS–WAXS pattern of T-monomer. (d) POM image, (e) DSC thermogram, and (f) SAXS–WAXS pattern of the melamine-core complex.



Figure 4. (a) Picture of the prepared supramolecular liquid crystal polymeric film. (b) FT-IR spectra and (c) SAXS–WAXS patterns of the melamine-core complex monomer and the corresponding polymeric film.

the integral value of the H_a signal at 6.20 ppm corresponded to 2 (Figure S11).

Mesomorphic Properties of T-Monomer and Melamine-Core Complex Monomer. The mesomorphic properties of T-monomer and melamine-core complex monomer were characterized by utilizing a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and combined small- and wide-angle X-ray scattering (SAXS–WAXS) measurements. As shown in Figure 3a, the POM image of T-monomer manifested a typical crystalline spherulite texture cooled from its isotropic phase. DSC thermogram showed a crystal-to-isotropic transition peak at 60.95 °C on heating (Figure 3b). The SAXS–WAXS pattern indicated plenty of crystalline peaks in the wide-angle region (Figure 3c). The above measurements revealed that Tmonomer had no liquid crystalline phase.

The melamine-core complex was a hydrogen-bonded supramolecular conjugated structure bearing nine flexible long chains. As can be seen in Figure 3d, a focal-conic fanshaped texture of the melamine-core complex was observed on cooling process under POM at room temperature. The DSC

thermogram indicated two enantiotropic phase transitions, which corresponded to the crystal-to-LC phase transition at 4.09 °C and the LC-to-isotropic phase transition at 69.56 °C on heating, respectively (Figure 3e). The SAXS-WAXS pattern of the melamine-core complex measured at room temperature showed a sharp and forceful scattering reflection with a *d*-spacing of 46.0 Å and two other weak peaks at 26.6 and 23.1 Å in the small-angle region, with the indexes as 100, 110, and 200 reflections. The reciprocal d-spacing of three reflections in the ratio $1:\sqrt{3:2}$ was related to structural characterization of the Col_h phase, with the lattice constant a =53.1 Å. Furthermore, the liquid-like order of the aliphatic alkyl tails at around 4.2 Å and $\pi - \pi$ stacking interactions with a periodicity of 4.0 Å were certified by the broad diffuse halo in the wide-angle region (Figure 3f). As a result, the above characterizations confirmed that the melamine-core supramolecular complex was a room-temperature enantiotropic discotic LC monomer.

Moreover, we performed a comparative experiment between three supramolecular complexes with different T-monomer/ melamine molar ratios (2:1, 3:1, and 4:1), which were



Figure 5. (a) FT-IR spectra and (b) SAXS–WAXS patterns of melamine-core polymeric materials before (with melamine) and after (without melamine) core removal through a hot DMSO treatment and after the readsorption of melamine.

investigated under POM. All the POM images except the one of the 3:1 molar ratio complex (Figure 3d) showed crystalline textures (Figure S12a,b). It is remarkable that despite none of the pure molecules (i.e., T-monomer and melamine) being liquid crystals, mesomorphic properties could be obtained from the supramolecular complex with an appropriate proportion between nonmesogenic molecules, which provided a solid proof for the formation of the supramolecular complex with a 3-to-1 T-monomer/melamine molar ratio.

Preparation of Supramolecular Liquid Crystal Polymeric Materials. UV-initiated free radical polymerization was applied to cross-link the supramolecular complex monomers. In a typical experiment, a mixture of the melamine-core complex monomer and 2.0 mol % of the photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide was melted and sandwiched between two glass substrates. After thermally annealed by cooling from its isotropic phase to LC phase at a rate of -0.1 °C min⁻¹, the mixture was irradiated under UV light (365 nm) at 30 °C for 10 h, which afforded a freestanding film with ca. 15 μ m thickness (Figure 4a). As illustrated in FT-IR spectra (Figure 4b), the polymerization of the complex monomer was verified by the absolute disappearance of the -CH=CH₂ in-plane bending vibration band at 1408 cm⁻¹. Moreover, acrylate polymerization was confirmed by the C-O-C asymmetric and symmetric stretching vibration bands of ester groups shifted prominently from 1296 to 1236 cm⁻¹ and from 1196 to 1165 cm⁻¹, respectively. In addition, it was critical that the photopolymerization did not damage the hydrogen-bonded structures and the combination modes on account of the main characteristic peaks of melamine and T-monomer substantially unchanged.

When it came to thermally annealing, the phase transition hysteresis and recovery were widely discussed, $^{21,52-60}$ which was of vital importance to the properties of discotic LCs. Mesophase recovery of hydrogen-bonded supramolecular LC monomer was an extremely slow process due to the considerable dissociation of hydrogen-bonded sites in the isotropic phase and the subsequent recombination into supramolecular complexes on the cooling process.⁵³ Rapid thermal anneal resulted in an incomplete restoration of liquid crystallinity and formation of nonmesomorphic complexes. For example, on cooling process at a rate of -1.0 °C min⁻¹, even though DSC data of the complex monomer indicated a short LC-to-isotropic transition temperature hysteresis with around 5.5 °C (Figure 3e), the scattering peaks of the Col_h arrangement in the small-angle region were unrecovered as shown in Figure S13. Hence, a cooling rate of -0.1 °C min⁻¹ was chosen to facilitate the change from viscous oil into mesomorphic solid of the complex, which resulted in the complete formation and recovery of the LC phase.

Most importantly, the thermal annealing and mesophase recovery brought about the molecule rearrangement and appropriate regulation of LC monomer to afford a hexagonal columnar order. Moreover, surface interaction of smooth glass could promote the orientational orders of discotic LCs.^{10,62} Furthermore, polymerization contributed tremendously to the fixation and maintenance of Col_h phase. As illustrated in Figure S14, POM images of three different regions showed the texture of the melamine-core complex before and after UV polymerization had little change, which implied that the hexagonal columnar microstructure could be retained. In addition, the SAXS-WAXS pattern of the polymeric film indicated the reciprocal of the scattering peaks from the *d*-spacing of the reflections in the small-angle region was in a ratio of $1:\sqrt{3}$, which confirmed that the Col_b arrangement of the polymeric film was formed and retained (Figure 4c). However, compared with the SAXS-WAXS pattern of the complex monomer, the corresponding polymeric film sample showed a slight shift and diffusion of the scattering peaks in the small-angle region, possibly due to the following facts: (1) The cross-linkage of terminal acrylate groups would shorten the diameter of the LC disc and the lattice spacings, which could also decrease the degree of Col_h order in the LC nanomaterials.^{3,48,49} (2) Oxygen or photoinitiators might induce side reactions, which could result in the perturbation of the LC assembly and order. (3) The viscosity and phase transition hysteresis of some discotic LC molecules could cause a slow and even incomplete recovery of mesophase in the thermal annealing process, which could also contribute to the decrease of LC arrangement in the polymeric film.

Removal of Melamine Cores. Because of the synergistic effect of nine hydrogen bonds inside the supramolecular complex, an effective removal of the melamine core was very challenging. Two main factors need to be considered: (1) The destruction of strong noncovalent binding might require harsh conditions, such as acid and base. (2) The transference of melamine to the solution relied on an efficient dissolvation, whereas the poor solubility of melamine increased the difficulty of core transfer, which drove the selection of a suitable solvent. Owing to the nonpolarity and hydrogen-bonded sites of melamine, plenty of solvents were screened (Table S1), and dimethyl sulfoxide (DMSO) with superb solubility of melamine was selected.



Figure 6. (a) Maximum UV-vis absorbance values of melamine and 1-aminopyrene along with the nanoporous material immersing time lengthened. (b) Melamine adsorption capacity of the nanoporous LCP material measured at different pH values (pH = 4, 7, and 10). (c) Cyclic adsorption tests of the nanoporous LCP material. (d) Melamine adsorption kinetics of the nanoporous LCP material based on the absorbance variation of melamine at 203 nm. (e) Lagergren first-order and (f) pseudo-second-order kinetic models of the nanoporous LCP material's uptake capacity of melamine.

Acidic or basic interactions, the common harsh conditions for core elimination, were then investigated. The LCP films were treated by concentrated hydrofluoric acids, hydrochloric acids, and sodium hydroxide solutions. However, these methods required a good deal of time (3–4 days) to achieve the removal and disrupted the ordered arrangement because of acid or alkali corrosion, in particular hydrolysis of ester group catalyzed by caustic soda (Figure S15 and Table S2; detailed characterizations are depicted in the Supporting Information).

Fortunately, a hot DMSO treatment achieved an efficient melamine removal without noticeable structure/alignment destruction. The polymeric material (0.40 mg) was stirred in 50 mL of DMSO at 160 °C for 10 h. FT-IR spectra revealed the disappearance of the melamine $-NH_2$ stretching vibration band at 3360 cm⁻¹ and the triazine -C=N stretching vibration band at 1551 cm⁻¹ and a notable decrease of the triazine ring deformation vibration band at 810 cm⁻¹ (Figure 5a). Moreover, X-ray photoelectron spectroscopy (XPS) showed the removal percentage of melamine reached 87.10% (Table S2), implying a high melamine elimination degree. The effective removal could be due to the fact that a slight hot effect ruptured hydrogen bonds⁴⁷ to reduce the restriction on melamine and enlarge the freedom degrees of melamine, and subsequently the excellent solubility of melamine in DMSO contributed to the core transference from polymeric materials to solution. Most importantly, the SAXS-WAXS pattern confirmed the resulting nanoporous polymer could retain the Col_b alignment after removal of melamine (Figure 5b), although the peak intensity at 31.4 Å decreased, probably due to the hot effect⁴⁷ and hole collapse.^{48,49} Furthermore, the primary signals of T-monomer in the polymer sample had no obvious difference, implying that the hot DMSO treatment did not interfere with the nanoporous film structure (Figure 5a). Overall, a hot DMSO treatment accomplished the retention of mesomorphic order and functionality in nanopores.

As illustrated in Figure S16a, the nanoporous material fabricated by the hot DMSO treatment possessed a high thermal stability with the initial thermal decomposition (5% weight loss) temperature at 378 °C, as demonstrated by thermogravimetric analysis (TGA). In addition, the nanoporous material was very stable even in harsh chemical conditions (e.g., acid, dilute alkali, oxidation or reduction environments) for 3 weeks, which were verified by the preservation of all the functionality peaks on FT-IR spectra and the scattering peaks on SAXS–WAXS patterns (Figure S16b,c).

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Selective Uptake of Melamine through Nanoporous Supramolecular Liquid Crystal Polymeric Materials. The small pore diameter, specific hydrogen-bonded sites, and strong systematic binding in the Col_h nanochannels of the nanoporous supramolecular LCP materials contributed to a series of superior properties, including selective and competitive uptake, adsorption in harsh environments, and recyclable adsorption. Moreover, the adsorption capacity and kinetics were further investigated to understand the adsorption dynamics and mechanism of the LCP materials.

To demonstrate the capability of the nanoporous supramolecular LCP materials for high-selective recognition and separation of melamine, a competitive uptake experiment between melamine (5.1 Å \times 5.1 Å, Figure S17a) and 1aminopyrene (APy, 4.8 Å \times 6.9 Å, Figure S18c) was performed. In general, both melamine (0.10 mM) and APy (0.10 mM) were dissolved in 2.00 mL of water/methanol (v/v, 1:19) solution, and a piece of the nanoporous LCP material was then immersed into the solution. 0.15 mL of such a solution was extracted and diluted by water to 2.70 mL, which was then examined by UV-vis spectroscopy. The obtained UV-vis spectra (Figure 6a and Figure S19a) showed an obvious absorbance decrease of melamine at 203 nm and unchanged absorbance of APy at 415 nm along with the immersing time lengthened. Although the APy molecule with smaller molecular radius and hydrogen-bonded site (-NH₂ functionality) should be able to enter into the nanochannels of the polymeric materials, they were still rejected by the nanochannels, which could be mainly ascribed to the hydrogen-bonding and spatial match difference between APy molecules and nanopores. For further proof of the LCP material's high-selective uptake of melamine, more adsorption experiments using diverse organic molecules with different charges and sizes, including anionic dye methyl orange (MO, 4.9 Å \times 11.8 Å), cationic dye methylene blue (MB, 5.1 Å \times 13.8 Å), and neutral molecule meso-tetra(p-aminophenyl)porphine (TAPP, 14.2 Å \times 14.2 Å), were studied (Figure S18). As illustrated in Figure S20, all the absorbances of MO, MB, and TAPP solutions were barely changed along with the immersing time lengthened. On the one hand, MO and MB molecules, although they could have accessibility to the nanochannels, were significantly precluded due to the uncharged nanopore surface, which revealed the exclusion of anionic/cationic organic molecules. On the other hand, TAPP with multiple -NH₂ functionalities was barely absorbed due to the size exclusion, which seemed to be essential for the selective uptake mechanism since smaller molecules (i.e., melamine) showed higher uptake capability, in comparison to those with larger molecular sizes.

The pH influence on the melamine uptake capacity of the supramolecular LCP material was further investigated. A piece of the nanoporous LCP material (0.55 mg, theoretically maximum uptake of 23.62 μ g melamine) was immersed in a melamine solution (water, 1.00 mL, concentration = 100 μ g mL^{-1} , 4.23 equiv to the maximum possible adsorption quantity) under magnetic stirring at different pH values (pH = 1, 4, 7, 10, and 13). In each experiment, 0.02 mL of the original solution was extracted and diluted to 2.70 mL. The concentration of the diluted solution and melamine uptake quantity were measured by UV-vis spectroscopy and calculated based on the UV absorbance vs melamine concentration standard curve, which showed a good linearity consistent with Lambert–Beer's law ($\varepsilon = 3.9186 \times 10^{-4} \text{ Lg}^{-1}$ cm^{-1}), as demonstrated in Figure S21. Here the adsorption capacity $(q_t, eq 1)$ was defined as how many milligrams of melamine was absorbed per gram of LCP material as a function of uptake time.

$$q_t = \frac{(C_a - C_b)V}{m} \tag{1}$$

where C_a and C_b are the initial and final concentrations of melamine (mg L⁻¹), V is the volume (L) of the melamine aqueous solution, and m is the mass of the nanoporous LCP material (g). As shown in Figure 6b, the nanoporous LCP material displayed a good melamine adsorption capacity even in harsh environments; the q value reached 10.42, 7.77, and 8.64 mg g⁻¹ at pH ~ 7, 4, and 10, respectively. When the pH value was set as either 1 or 13, the absorption peak at ca. 203 nm in the melamine solution could not be observed by UV–vis spectroscopy because melamine was hydrolyzed under the strongly acidic or basic conditions and converted into cyanuric acid. Nonetheless, the nanoporous supramolecular LCP material demonstrated a stable uptake capacity over a broad range of pH values (pH 4–10).

The recyclable uptake performance of the nanoporous LCP material was elucidated by measuring the percentage of the occupied nanopores (occupation degree) in each melamine uptake process. In detail, a small piece of the nanoporous LCP material (0.38 mg) was immersed in a concentrated solution of melamine (water, 1.00 mL, concentration = 70 μ g mL⁻¹, 4.29 equiv to the maximum possible adsorption quantity), 0.02 mL of such a solution was extracted and diluted to 2.70 mL, which was further investigated by UV-vis spectroscopy. The concentration of the diluted solution and melamine uptake quantity were calculated based on the standard curve (Figure S21). Theoretically, a full refill of the Col_{h} nanochannels of the LCP material would take 16.32 μ g of melamine. When the first adsorption equilibrium reached, 9.52 μ g of melamine was absorbed, which accounted for 58.3% of occupied nanopores, as shown in Figure 6c. After melamine removal, the second and third adsorption capacities of the nanoporous material were 8.50 and 8.21 μ g, and the occupation degrees were calculated as 52.1% and 50.3%, respectively, which showed a good recyclable adsorbing performance.

To better understand the uptake phenomena and process dynamics, the melamine adsorption kinetics and mechanism of the nanoporous LCP material were further studied. As can be seen in Figure 6d and Figure S19b, melamine in the diluted solution was adsorbed by the nanoporous LCP material as indicated by UV absorbance decrease at 203 nm spectrophotometrically along with the extended time. A fast absorption process occurred in the first 96 h, possibly due to the presence of a vast amount of hydrogen-bonded sites on the nanochannel surfaces and a large concentration gradient between the solution and the adsorbent at the beginning. The dynamics platform with the maximum uptake capacity corresponding to the adsorption equilibrium was eventually achieved after 240 h.

The quantitative and theoretical analysis of the melamine uptake data was expressed by fitting the adsorption capacity (q_t) values to the Lagergren first-order (eq 2) and pseudo-second-order (eq 3) kinetic models,⁶³ whose equations are presented as

$$q_t = q_e (1 - e^{-k_{ad}t})$$
(2)

$$\frac{t}{q_t} = \frac{1}{k_{\rm ad} q_{\rm e}^2} + \frac{1}{q_{\rm e}} t$$
(3)

where q_e is the maximum capacity of melamine adsorbed at equilibrium, *t* is the uptake time, and k_{ad} is either the Lagergren first-order (h⁻¹) or pseudo-second-order (g mg⁻¹ h⁻¹) kinetic constant.

The resulting first- and pseudo-second-order kinetic curves for absorbing melamine were calculated by the linear regression q_t vs t and t/q_t vs t, respectively, and illustrated in Figure 6e,f. The correlation coefficient ($R^2 = 0.99939$) for the utilization of the pseudo-second-order model ($q_e = 14.61$ mg g^{-1} , $k_{ad} = 7.52 \times 10^{-4}$ g mg⁻¹ h⁻¹) confirmed that this model fitted the kinetic data more accurately than the first-order kinetic model for the real-time detection of the adsorption capacity of the nanoporous supramolecular LCP material.

CONCLUSION

In conclusion, we reported a nanoporous LCP material built on melamine/thymine-derivative supramolecular structure, which could specifically recognize and selectively absorb melamine. Such a material presented a stable and recyclable melamine adsorption capacity over a broad range of pH environments (pH 4–10). To the best of our knowledge, this work was the first example using the imidodicarbonyl functionality (thymine derivative) as the recognition sites of supramolecular discotic LCP matrices, capable of breaking some highly self-complementary hydrogen-bonded units (e.g., melamine), which were extremely difficult for the widely used carboxylic acid-type discotic LCs (e.g., 3,4,5-trialkoxybenzoic acid) to competitively recognize and bind. We hope this work brings a new perspective for the development and application of supramolecular nanoporous materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00322.

Instrumentation descriptions, detailed experimental procedures, and materials characterization (PDF)

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Notes

The authors declare no competing financial interest.

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