Composition-Driven Structural Modulation and Guest-Induced Nanotemplate Effects of the Host–Guest Complexes Made by a Unimolecular Q-Clip

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ABSTRACT: The composition of a self-assembly system has long been an essential factor that governs the resulting supramolecular structures. Nevertheless, due to the rigorous demands of structural compatibility in host–guest chemistry, the molar ratio of host–guest mixtures has not been applied as a significant factor in modulating the supramolecular structures of host–guest complexes. In this study, via using a novel unimolecular quaternary clip (Q-clip) as the host molecule and pyrene as the guest molecule and a nanotemplating reagent, we discovered that the changes in the molar ratios of the Q-clip:pyrene mixtures resulted in the structural modulation of the host–guest complexes. Supramolecular lamellae made by the 1:4 Q-clip:pyrene mixture and a hexagonal columnar phase (Colh) made by the 1:8 Q-clip:pyrene mixture were identified by the 1D powder and 2D fiber WAXS characterizations. Time-resolved synchrotron X-ray characterization and thermal analysis further showed that removing the easily sublimed guest molecules (pyrene) via thermal annealing simply hollowed out the supramolecular structures without damaging the supramolecular scaffolds made by the Q-clips. Pyrene is thus a nanotemplating reagent that can be used to create the hollowed-out 2D lamellar and 1D cylindrical scaffolds of Q-clips. The study thus gave a novel example of a host–guest mixture that is able to carry out composition-driven structural modulation and guest-induced nanotemplates. The finding broadens the horizon of host–guest chemistry and may inspire more nanoinnovation.

INTRODUCTION

In multicomponent systems, the molar fraction of the constituent components is an essential factor that governs physical properties, physical transitions, and self-assembly of a system. Changes in the molar fractions of the constituent components alter the stabilities of the physical states of a system and result in changes in the self-assembly morphologies. For example, manipulating the molar fraction of the constituent components in block copolymers and giant molecules has enabled the system to create supramolecular architectures, including 1D nanorods, 2D nanosheets, and 3D interpenetrating networks.

Host–guest complexes are a representative bicomponent (or multicomponent) system in supramolecular chemistry. Geometry and symmetry of the constituent components typically determine the final supramolecular structures of the host–guest mixtures since the synthetic host and guest molecules commonly have complementary shapes and can coassemble via molecular recognition. Particularly, inclusion complexes of polycyclic aromatic hydrocarbons as guest molecules attract great interest to find a way to solve the environmental issue of persistent organic pollutants. However, although research studies have shown that linear, trigonal, and tetrahedral guest molecules can assemble with synthetic hosts to give 1D to 3D supramolecular architectures, these supramolecular architectures only could form in a specific host–guest composition and cannot be modulated by changing the molar ratio of the host–guest mixtures. There remains no report demonstrating the composition-driven structural modulation of host–guest mixtures to the best of our knowledge.

In addition, the development of porous materials with ordered and tailorable architectures is a subject of intense research. Supramolecules with ordered self-assembly structures and micropores have useful applications in areas such as gas storage, separation, and sensing. Cross-linkable amphiphilic monomers with sacrificial templating molecules have been first used by Kim and co-workers by coassembling them...
into an ordered thermotropic phase and then cross-linking to form the nanoporouss host materials after removing the templating molecules. The presence/absence of guest molecules switch the supramolecular architectures of the host materials has further been extensively studied for the past two decades.

Herein, we demonstrate a novel host–guest system, in which the host–guest composition (Figure 1a) can modulate the noncovalent interaction (Figure 1b) in the mixture and thus program the resultant supramolecular architectures. Figure 1c shows the chemical structure of the host molecule, Q-clip. It is a unimolecular quaternary clip (Q-clip) that owns eight N-hexyl-1,4,6,8-naphthalene diimide (NDI) as the capture units. Meanwhile, pyrene serves as a guest molecule and a nanotemplating reagent to facilitate the charge transfer (CT) interactions and coassemble with the Q-clip. The types of noncovalent interactions in the Q-clip:pyrene mixtures can be adjusted by the composition of the mixture. As shown in Figure 1a,b, both the NDI-NDI π–π interaction and NDI-pyrene CT interaction are present in the 1:4 Q-clip:pyrene mixture (denoted as Q-clip:pyrene4), whereas there is only NDI-pyrene CT interaction in the 1:8 Q-clip:pyrene mixture (denoted as Q-clip:pyrene8). The balance of the noncovalent interactions in the system was found to be affected by the composition. As a result, structural characterization results show that the Q-clip:pyrene4 forms a lamellar phase that contains 2D nanosheets of a T8 cage of polyhedral oligomeric silsesquioxane (POSS) units separated by the layers of the π-stack of the NDI-pyrene and NDI-NDI mixtures, whereas the Q-clip:pyrene8 forms a hexagonal columnar phase (Colh) that contains POSS units stacked into 1D nanorods surrounded by the helices of the NDI-pyrene CT complexes. Moreover, pyrene can further be used as the nanotemplating reagent to create micropores in templated Q-clips because of its low sublimation temperature. The thermal analysis and in situ WAXS measurements confirmed that after removing the pyrene template by thermal annealing, the templated Q-clip maintains the structural integrity of the supramolecular scaffolds and results in the ordered microporous materials. The study thus enables the composition to govern the self-assembly pathways of a host–guest mixture and provide a facile procedure to prepare ordered microporous scaffolds, which broadens the horizons of host–guest chemistry.

### RESULTS AND DISCUSSION

The Q-clip was synthesized according to Scheme S1. The capture unit, HA-NDI, was prepared in two steps. First, monoimidation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) was carried out by reacting NDA with hexylamine in dimethyl formamide (DMF) at 110 °C to give Hex-NMI in 50% yield. Further reaction of Hex-NMI and allylamine in DMF at 110 °C gave HA-NDI in 55% yield. Finally, by reacting the excess equivalent of the capture unit (HA-NDI) with the core unit (octakis(dimethylsiloxyl)substituted polyhedral oligomeric silsesquioxanes, POSS-SiH) via the hydrosilylation reaction, the Q-clip was obtained in 45% yield. The products were characterized by 1H NMR, 13C NMR, and mass spectrometry, as shown in Figures S1–S10.

1H NMR titration experiments were performed (Figure 1d) to investigate the host–guest complexion between Q-clip and pyrene in solution. The Q-clip:pyrene mixture gave a spectrum that is different from those of pure Q-clip and pure pyrene, indicating that the fast-exchange process on the NMR time scale did take place due to the CT-complexation of Q-clip and pyrene molecules in CDCl3 (Figure 1d-II). The NDI proton signals of Q-clip are shifted upfield by 0.08 ppm due to the electron donation from electron-rich pyrene. Meanwhile, the upfield shifts of pyrene protons by 0.04 ppm suggest the formation of inclusion complexes via catching the pyrene...
Two different mixtures are completely different in Figure 2a,b, respectively. The 1D powder SAXS/WAXS patterns of the two mixtures are shown in Figure 2a,b, respectively. After the addition of pyrene, a new broad CT absorption band at 500 nm appeared, indicating the CT–π–π stacking interaction coexist in the solid mixture of Q-clip:pyrene and pyrene. A continuously increasing intensity of this CT band resulted from the increasing concentration of supramolecular complexes. These results demonstrate that the favorable CT interactions would draw the Q-clip and the pyrene molecules closer to each other to form supramolecular complexes in solution.

In the condensed phase, noncovalent interactions including POSS–POSS interaction, NDI–NDI π–π interaction, and NDI–pyrene CT interaction coexist in the solid mixture of Q-clip and pyrene. The balance of different interaction types governs the self-assembly dynamics and the final supramolecular structures. Ideally, to form a complete alternating π–π stacking of the NDI-pyrene CT complexes, the molar ratio of NDI and pyrene should be 1:1. Thus, it requires a 1:8 molar ratio of a Q-clip:pyrene mixture to provide the necessary condition for the formation of a complete NDI-pyrene π-stacking in the mixture, whereas the insufficient supply of pyrene results in the presence of both NDI-NDI and NDI-pyrene π-stacking in the mixture. We thus speculated that changing compositions of the Q-clip:pyrene mixtures could alter the aromatic interactions in the system and may result in the composition-driven structural modulation, as illustrated in Figure 1a. To examine the validity of this idea, the self-assembly structures of the 1:4 mixture (Q-clip:pyrene) and 1:8 mixture (Q-clip:pyrene) of the Q-clip and pyrene were studied by XRD diffractometry. The 1D powder SAXS/WAXS patterns of the two mixtures are shown in Figure 2ab, respectively. The diffraction patterns of the two mixtures are completely different from those of the pure components (Q-clip and pyrene) shown in Figures S11 and S12. Two diffraction peaks of Q-clip:pyrene observed at the scattering vectors (q) = 0.31 and 0.62 Å\(^{-1}\) show a q ratio of 2:1, whereas three diffraction peaks of Q-clip:pyrene observed at q = 0.18, 0.32, and 0.36 Å\(^{-1}\) show a q ratio of 1:√3:2. The results indicate that Q-clip:pyrene forms host–guest complexes that self-assembled into a supramolecular lamellar structure, while the host–guest complexes of Q-clip:pyrene self-assembled into a hexagonal columnar phase (Col\(_h\)). Note that the electron density of the aromatic domains could be close to the electron density of the POSS domains in the lamellar structure of Q-clip:pyrene, which causes the system absences of the (010) and (030) diffractions. Changing the compositions of the Q-clip:pyrene mixtures altered the aromatic interaction in the system and resulted in a rare example of composition-driven structural modulation of host–guest chemistry in the bulk assembly.

To reveal more detailed structures in the mixtures, oriented samples of Q-clip:pyrene and Q-clip:pyrene were grown in the apparatus shown in Figure S13 and used to obtain the high-quality 2D fiber WAXS patterns shown in Figure 2c,d. The (020) and (040) diffractions from the lamellar structure of Q-clip:pyrene and the (200), (110), and (300) diffractions from the Col\(_h\) phase of Q-clip:pyrene were found along the meridian, whereas the diffraction from the π-stacking was found along the equator of the 2D fiber WAXS patterns. The results indicate that the aromatic moieties in the mixtures were π-stacked with a d-spacing of 3.50 Å along the growth axis (c-axis) of the fiber samples. Moreover, perpendicular to the c-axis, the host–guest complexes of Q-clip:pyrene further stack into a 2D lamellar structure, whereas the supramolecular columns of Q-clip:pyrene pack into a 2D hexagonal lattice as illustrated in Figure 2e,f. The d-spacing of the lamellar packing (\(d_{010}\)) was deduced to be 40.4 Å from the (020) diffraction found in Figure 2c, and the d-spacing of the hexagonal lattice (\(d_{1100}\)) was deduced to be 35.2 Å from the (100) diffraction found in Figure 2b.

An additional diffraction arc of Q-clip:pyrene was found nearly at the (040) diffraction but deviated slightly from the meridian. This diffraction cannot be incorporated into the b*-c* reciprocal lattice. In the seven lattice systems, the monoclinic lattice has its b and c axes perpendicular to each other (\(\alpha = 90^\circ\)), but its a and c axes are not perpendicular to each other (\(\beta \neq 90^\circ\)). Thus, in the 2D fiber diffraction of a monoclinic lattice, when the c* axis is placed along the equator, the b* axis is on the meridian, but the a* axis is deviated from the a-axis.

Figure 2. 1D powder SAXS/WAXS patterns of (a) Q-clip:pyrene and (b) Q-clip:pyrene. The 2D fiber WAXS patterns of (c) Q-clip:pyrene and (d) Q-clip:pyrene. The lattice models of (e) Q-clip:pyrene and (f) Q-clip:pyrene.
meridian. Using this crystallographic concept, the unsolved diffraction of Q-clip:\textsuperscript{pyrene}_{8} was assigned as the (100) diffraction of the lamellar structure, and \(d_{100}\) was deduced to be 11.0 Å. By combining the structural information along the \(a\) and \(c\) axes, the \(ac\) projection of the lamellar structure was revealed and shown as the “top view” in Figure 2e. More details regarding the correlation between the \(a^*c^*\) reciprocal lattice in the 2D WAXS pattern and the \(ac\) projection of the lattice in real space can be found in Figure S14. It can be found that the POSS core units pack into 2D nanosheets that contain the POSS units separated by 11.0 Å along the \(a\) axis and 10.5 Å (\(\sim 3\ d_{ac}\)) along the \(c\) axis.

The structural modulation caused by the additional 4 equiv of pyrene can be further investigated by comparing the diffractions from the \(\pi\)-stacking of Q-clip:\textsuperscript{pyrene}_{4} and Q-clip:\textsuperscript{pyrene}_{8}. The diffraction arc from the \(\pi\)-stacking was found to be much broader in Q-clip:\textsuperscript{pyrene}_{4} by using the Scherrer equation (\(L_c = \frac{2NK}{\Delta_\theta}\) where \(L_c\) is the correlation length of a periodic structure, \(\Delta_\theta\) is the full width at maximum of the \(\pi\)-diffraction peak, and \(K\) is the shape factor (here we use 1.0)), the \(L_c\) values of the \(\pi\)-stacking were estimated to be 6.4 nm in Q-clip:\textsuperscript{pyrene}_{4} and 18.7 nm in Q-clip:\textsuperscript{pyrene}_{8}. Figure S15 provides the illustration that relates the \(d_{ac}\) with the \(L_c\) and the packing models. In the figure, it can be found that the \(\pi\)-stacking keeps its long-ranged order in average lengths of ca. 18 \(d_{ac}\) in the lamellar phase of Q-clip:\textsuperscript{pyrene}_{4} and ca. 53 \(d_{ac}\) in the Col\(_b\) phase of Q-clip:\textsuperscript{pyrene}_{8}. In the literature, the ND\textsubscript{I}-pyrene CT complexes were reported to form a face-to-face, alternating \(\pi\)-stacking\textsuperscript{29} which is different from the crystal structure of pure NDI that has ND\textsubscript{I}-NDI \(\pi\)-stacking.\textsuperscript{30} Since Q-clip:\textsuperscript{pyrene}_{4} does not have sufficient equivalent of pyrene to form the complete ND\textsubscript{I}-pyrene \(\pi\)-stacking, the broader diffraction arc and the shorter \(L_c\) found in Q-clip:\textsuperscript{pyrene}_{4} were thus attributed to the presence of the ND\textsubscript{I}-NDI \(\pi\)-stacking, which cut short the correlation length of ND\textsubscript{I}-pyrene \(\pi\)-stacking. On the contrary, Q-clip:\textsuperscript{pyrene}_{8} has the correct composition to form the complete and continuous ND\textsubscript{I}-pyrene \(\pi\)-stacking in the mixture. The complete ND\textsubscript{I}-pyrene \(\pi\)-stacking not only resulted in the sharper diffraction arcs but also significantly changed the self-assembly structure of the host–guest complexes. The additional pyrene molecules strengthen the aromatic interaction and occupy the extra space in the supramolecular structure, which forbid the formation of the 2D POSS nanosheets found in the lamellar structure of Q-clip:\textsuperscript{pyrene}_{4}. Instead, in the Col\(_b\) phase of Q-clip:\textsuperscript{pyrene}_{8}, 1D POSS nanorods surrounded by the continuous \(\pi\)-stack of ND\textsubscript{I}-pyrene complexes were formed along the growth axis (\(c^*\)).

The packing model of Q-clip:\textsuperscript{pyrene}_{8} along the \(c^*\) axis is also complicated since there are two major diffractions observed along the \(c^*\) axis in Figure 2d. The strongest one was assigned as the diffraction from the ND\textsubscript{I}-pyrene \(\pi\)-stacking (\(d_{c^*\alpha} = 3.5\) Å), and the second one observed at \(q = 0.72\) Å\(^{-1}\) was assigned for the 1D POSS-POSS stacking (\(d_{\text{POSS-POSS}} = 8.7\) Å). It should be noted that in the continuous ND\textsubscript{I}-pyrene \(\pi\)-stacking, the pyrene guest molecules can be placed either within the cavity of a Q-clip or between two neighboring Q-clips. Thus, for every four steps of \(\pi\)-stacking, the pyrene guest molecules will be found to be placed in a similar environment. This may be the reason why one additional weak diffraction at \(q = 0.44\) Å\(^{-1}\), representing a periodicity of 4 \(d_{c^*\alpha}\) was also observed along the equation of Figure 2d. The diffractions of the POSS-POSS stacking and continuous NDI-pyrene \(\pi\)-stacking were both found on the \(c^*\) axis. To accommodate the two types of packings, which have different periodic \(d\)-spacings (\(d_{\text{POSS-POSS}} < 4\ d_{c^*\alpha}\)), the continuous ND\textsubscript{I}-pyrene \(\pi\)-stacking was proposed to twist around the 1D POSS nanorods that contain continuous 1D POSS-POSS stacking (Figure 2f).

The completely different supramolecular structures of Q-clip:\textsuperscript{pyrene}_{4} and Q-clip:\textsuperscript{pyrene}_{8} indicate that the 1:8 Q-clip:\textsuperscript{pyrene} composition perfects the ND\textsubscript{I}-pyrene \(\pi\)-stacking at the cost of sacrificing the lateral POSS-POSS interactions, which degrades the 2D POSS sheet and results in the 1D POSS nanorod in Q-clip:\textsuperscript{pyrene}_{4}. In liquid crystal (LC) materials, lamellar structures were found in the smectic phases formed by rod-like mesogens, whereas the columnar phases were reported for discotic mesogens.\textsuperscript{31} Nevertheless, formation of both smectic phase and columnar phase by a single type of LC mesogen (rod-like or discotic) is difficult. Via the composition-driven structural modulation, the host–guest complexes of Q-clip:\textsuperscript{pyrene} were found to behave like a rod-like mesogen to self-assemble into a lamellar structure at the composition of 1:4, while they behave like a discotic mesogen to self-assemble into the Col\(_b\) phase. The supramolecular chemistry of the Q-clip:\textsuperscript{pyrene} mixture is thus unique among the LC materials and host–guest complexes.

The lamellar and columnar phases of the Q-clip:\textsuperscript{pyrene} mixtures can be further hollowed out to create micropores by subliming the pyrene guest molecules via thermal annealing. In Figure 3a, the thermal gravimetric analysis (TGA) thermograms show the Q-clip is thermally stable and has no weight loss in the temperature range from 40 to 300 °C. On the contrary, pyrene in the Q-clip:\textsuperscript{pyrene} mixtures starts to sublime at around 150 °C, resulting in the 16.7% weight loss for Q-clip:\textsuperscript{pyrene}_{4} and 28.1% weight loss for Q-clip:\textsuperscript{pyrene}_{8}. The weight loss matches well with the weight percent of pyrene in Q-clip:\textsuperscript{pyrene}_{4} (16.4%) and Q-clip:\textsuperscript{pyrene}_{8} (28.1%), indicating that pyrene can be completely removed from the host–guest complexes after the thermal treatment. In Figure 3b, the differential scanning calorimetry (DSC) thermograms show the sublimation temperatures of pyrene in the two Q-clip:\textsuperscript{pyrene} mixtures and echo the 2D fiber WAXD results in Figure 2c,d because the higher sublimation temperature of pyrene in Q-clip:\textsuperscript{pyrene}_{4} (193 °C) than in Q-clip:\textsuperscript{pyrene}_{8} (160 and 191 °C) suggests that pyrene in the complete ND\textsubscript{I}-pyrene CT complex of Q-clip:\textsuperscript{pyrene} is less volatile and more difficult to sublime. Moreover, the two broader and separated endothermic peaks of Q-clip:\textsuperscript{pyrene}_{4} suggest that in the lamellar structure, the pyrene molecules...
may be distributed in two different microenvironments, which causes the different volatilities of the pyrene guest.

The structural transformation of Q-clip:pyrene$_4$ and Q-clip:pyrene$_8$ during the sublimation of pyrene was further investigated by the in situ WAXS measurements. As shown in Figure 4a,b, the WAXS patterns were recorded when the samples were heated by 15 °C min$^{-1}$ from room temperature. Structural transformations observed from the WAXS patterns become obvious when the sample temperature approaches the sublimation temperature of pyrene (ca. 150 °C). The changes in the diffraction patterns indicate that the supramolecular lamellar scaffold of Q-clip:pyrene$_4$ and columnar scaffold of Q-clip:pyrene$_8$ remain intact, but the NDI-pyrene π-stacking was degraded due to the sublimation of pyrene since the diffraction intensities of the (002) and (004) diffractions of Q-clip:pyrene$_4$ and those of the (200), (110), and (300) diffractions of Q-clip:pyrene$_8$ were retained, but the diffraction intensity of the π-stacking at $q = 1.8$ Å$^{-1}$ diminished at temperatures above 160 °C.

Figure 4c,d shows the 2D WAXS patterns of the thermally annealed Q-clip:pyrene$_4$ and Q-clip:pyrene$_8$ after annealing at 140 °C under vacuum for 12 h. The two samples now contain no pyrene but still keep clear (020), (040), (060), and (080) diffractions from the lamellar scaffold and clear (200), (110), and (300) diffractions from the columnar scaffold. Although the removal of pyrene caused the expansion of the lamellar d-spacing ($d_{(002)}$) to 43.2 Å and the hexagonal lattice ($d_{(110)}$) to 39.9 Å (illustrated in Figure 4e,f), the 2D WAXS patterns further prove that the Q-clip can maintain the supramolecular scaffolds after removing pyrene. The two thermally annealed samples thus can be considered as the "lamella-templated Q-clip (LT Q-clip)" and "column-templated Q-clip (CT Q-clip)" prepared via hollowing out the lamellar structure of the Q-clip:pyrene$_4$ and the Col$_6$ structure of the Q-clip:pyrene$_8$.
respectively. In the 2D WAXS patterns, it is also evident that at the equator, the diffraction intensity from the \( \pi \)-stacking of the two samples has significantly decayed because there are no more NDI-pyrene CT complexes to give a periodic \( d \)-spacing of 3.50 Å. Nevertheless, the periodic structures made by the 2D and 1D stack of the POSS units are retained because similar to Q-clip:pyrene, the LT Q-clip gave an additional diffraction next to its (040) diffraction (\( d \)-spacing = 11.4 Å, see Figure 4c), and just like Q-clip:pyrene, the CT Q-clip delivers the diffraction of POSS-POSS stacking along the equator (see Figure 4d). An additional diffraction of the LT Q-clip next to the (020) diffraction has a \( d \)-spacing of 15.9 Å and is assumed to be the diagonal POSS-POSS distance as illustrated in Figure 4e. Thus, the noncovalent interaction among the POSS units of the Q-clips may allow the Q-clip molecules to maintain the structural integrity of the lamellar and columnar supramolecular scaffolds, while the sublimation of pyrene hollows out the host-guest complexes and makes pyrene a nanotemplating reagent.

Because the templated Q-clips were supposed to contain micropores in their aromatic domains after removing the pyrene templating reagent, we further investigated the porosity of templated pyrene Q-clips and Q-clip via nitrogen adsorption/desorption analysis (Figure 5a). While the \( N_2 \) isotherm curve of the untemplated Q-clip revealed much higher absorbed volume of \( N_2 \) at a broad pore size distribution at 45 nm (Figure S16), both the adsorption capacity of LT Q-clip and CT Q-clip declined dramatically. These results indicated that Q-clip formed more compact structures after it was lamella- or column-templated. Considering that the sublimation of pyrene from the NDI-pyrene CT complexes may only leave rectangular holes with a pore size less than 1 nm and a shape similar to pyrene, it is reasonable that the micropores in the templated Q-clips were not measured by the nitrogen adsorption/desorption experiment. Nevertheless, the ordered micropores in the templated Q-clips seem to be revealed by the \( in situ \) WAXS patterns (Figure 4a,b), as a new diffraction peak with a \( d \)-spacing of 5.9 Å appeared when the diffraction of the \( \pi \)-stacking at \( q = 1.8 \) Å\(^{-1}\) diminished due to the removal of pyrene at temperatures above 150–160 °C. The periodicity of 5.9 Å could come from the averaged distance of the NDI units in the templated Q-clips after the removal of pyrene. The periodicity is big enough to accommodate \( \pi \)-conjugated guests, so the templated Q-clips may act like a nanobookshelf that can store \( \pi \)-conjugated guests into its ordered micropores. To validate this possibility, both LT Q-clip and CT Q-clip were stored in a glass vial that contained vaporized pyrene molecules for 4 days (the apparatus is shown in Figure S17). The reappearance of the diffraction at \( q = 1.8 \) Å\(^{-1}\) on the equator of the 2D WAXS patterns shown in Figure 5b confirmed that the LT Q-clip can retake the vaporized pyrene guests to restore the NDI-pyrene \( \pi \)-stacking. Thus, the LT Q-clip is similar to a nanobookshelf that contained ordered micropores with a pore size less than 1 nm. In contrast, the diffraction of the NDI-pyrene \( \pi \)-stacking was not restored in the CT Q-clip after the same procedure, indicating that the structure of the CT Q-clip was too compact for the re-entry of the pyrene guests.

\[ \text{CONCLUSIONS} \]

In this work, we achieved composition-driven structural modulation and prepared lamella-templated and column-templated microporous scaffolds via simply coassembling and thermal annealing the mixtures of a novel host (Q-clip) and a sublimable guest (pyrene). Changing the compositions of the Q-clip:pyrene mixture was examined as the key factor to manipulate the balance of the noncovalent interactions and consequently the final supramolecular structures of the host–guest mixtures. The supramolecular structures were characterized by 1D powder SAXS/WAXS and 2D fiber WAXS. It was found that the insufficient supply of pyrene resulted in the incomplete formation of the NDI-pyrene CT complexes, and consequently, the 1:4 mixture (Q-clip:pyrene\(_4\)) formed a lamellar phase that contained the 2D nanosheets of POSS units. In contrast, the sufficient supply of pyrene resulted in the complete formation of the NDI-pyrene CT complexes, so the 1:8 mixture (Q-clip:pyrene\(_8\)) formed a \( \text{Col}_h \) phase that contained the 1D nanorods of POSS units. Moreover, the TGA, DSC, and \( in situ \) WAXS results indicated that the Q-clip in Q-clip:pyrene\(_4\) and Q-clip:pyrene\(_8\) can maintain the structural integrity of the supramolecular scaffolds while pyrene sublimes away from the host-guest complexes. The sublimation process thus hollowed out the lamellar structure of the Q-clip:pyrene\(_4\) and the \( \text{Col}_h \) phase of the Q-clip:pyrene\(_8\) and left the LT Q-clip and CT Q-clip behind as the ordered microporous lamellar and columnar scaffolds. The 2D WAXS results further revealed that LT Q-clip acted like a nanobookshelf that could reload pyrene into its micropores, while the structure of the CT Q-clip was too compact for pyrene to enter its micropores. The unique coassembly behaviors of the Q-clip:pyrene mixtures thus make composition an important and useful factor to diversify the supramolecular structures of the host–guest complexes. Moreover, taking advantage of the robust supramolecular scaffolds and the easily sublimed guest, our study also provides a facile nanotemplating technique for the further development of ordered microporous materials.

\[ \text{ASSOCIATED CONTENT} \]

\[ \text{Supporting Information} \]

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c00947.

Complete descriptions of experimental procedures, including the synthesis of Q-clip, X-ray structure determination, and illustration of sample preparation methods (PDF).

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