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Adaptive molecular quaternary clips made with pyrene functionalized polyhedral oligomeric silsesquioxane†

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Evolving synthetic molecules toward complex structures is a major goal in supramolecular chemistry. Increasing the number of clips in a unimolecular multi-clip (UMC), although vital to elevate the complexity of supramolecular architectures, often prevents the UMC from forming host–guest complexes in the bulk phase. To overcome this difficulty, adaptive chemistry was applied to develop a novel adaptive unimolecular quaternary clip (**Q-clip**). The **Q-clip** is intrinsically amorphous, but self-organizes with exclusively 4 eq. of allosteric activators (**NDI**) to form the **Q-clip** : **NDI**₄ complexes and a supramolecular lamellar structure in the bulk. The adaptive assembly is fast and allows us to locate the adaptive assembly area of **Q-clip** : **NDI**₄ complexes in the amorphous **Q-clip** film. Our results provide new insights into the design of adaptive UMCs for the evolution toward complex structures and supramolecular functional materials.

Host–guest chemistry has been a major topic in supramolecular chemistry since the concept was established in the 1980s.¹ Through the precise control over geometrical complementary and the non-covalent interactions between hosts and guest molecules, host–guest chemistry has been applied for mimicking biological processes, developing nanotechnology, and materials science.^{2–4} Molecular clips are one major type of host molecules.⁵ Made with pairs of capture units connected to a linker unit, molecular clips pinch guests by their capture units to form host/guest complexes.⁵ The facile synthesis and high solubility of molecular clips also make them versatile building blocks for supramolecular architectures.⁶

Increasing the number of the binding sites of a host molecule is essential to evolve synthetic molecules toward complex structures.⁷ Although molecular di-clips have demonstrated the ability to form more complex supramolecular structures than mono-clips,^{8–11} further increases in the number of clips in unimolecular multi-clips (UMC) remain elusive. Particularly in the bulk phase, although Nolte *et al.* pointed out that a bulk assembly of molecular clips is the basis for developing molecular materials with tunable properties, only very few mono-clips,^{11,12} and no di-clips or UMCs demonstrated host–guest assembly in the bulk phase.

Bulk self-organization of UMCs is difficult due to the high structural complexity of UMCs. To host *N* guest molecules, a UMC requires 2 *N* capture units.⁵ For example, a unimolecular quaternary clip (**Q-clip**) requires 8 capture units to host 4 guest molecules. Although star-molecules or dendrimers provide sufficient capture units for a UMC, our previous study showed that high conformational freedom complicates the self-organization pathways.^{13–15} To form ordered bulk structures, these molecules have to sort their high number of conformational isomers into suitable ones to self-organize. Therefore, a large number of capture units could make self-organization too complicated to occur and result in only an amorphous phase.

In this study, we developed an amorphous **Q-clip** that self-organizes in the bulk phase via adapting to guest molecules. As shown in Fig. 1, the **Q-clip** is an eight-arm-star giant molecule with 8 pyrene capture units connected to a polyhedral oligomeric silsesquioxane (POSS) core.¹⁶ The diameter of POSS (*ca.* 0.7 nm) is about 2 times the *d*-spacing of π – π stacking ($d_{\pi-\pi} \sim 0.35$ nm), which may create suitable space to accommodate a conjugated guest molecule. Although synthetic methods for octa-substituted POSSs have been established in the literature,^{17–19} the host–guest chemistry of octa-substituted POSS has not yet been developed. To reduce the conformational complexity of the **Q-clip** and enable the host–guest assembly, *N,N'*-dihexyl-1,4,6,8-naphthalene diimide (**NDI**) was used as a positive allosteric effector to unify the conformers of the **Q-**

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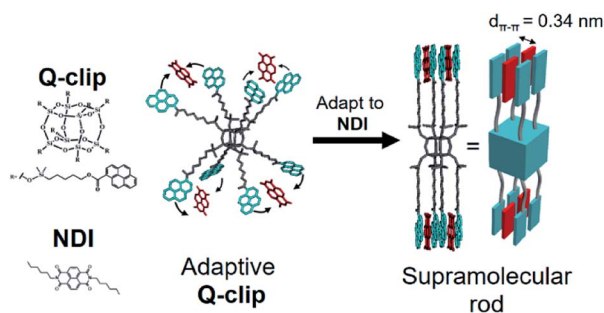


Fig. 1 The schematic representation for the conformational change of the **Q-clip** by the host-guest interaction.

clip.²⁰ The strong charge transfer (CT) interaction²¹ between the pyrene capture units of the **Q-clip** and the **NDI** guests is utilized to drive the adaptive self-organization of the **Q-clip** : **NDI** mixtures.^{22,23} Our results show that adequate geometrical arrangement of the capture units, suitable host/guest interaction, and adaptiveness of the UMC are essential for the design of UMCs that can self-organize in the bulk phase.

The **Q-clip** and **NDI** were synthesized according to Scheme S1.† The products have been fully characterized by ¹H NMR, ¹³C NMR, and mass spectrometry, as shown in Fig. S1–S9.† The geometrical effect of the POSS core can be seen in fluorescence (FL) titration experiments. In Fig. 2a, the **Q-clip** gives strong excimer FL but weak unimer FL, whereas the pyrene capture unit shows only the unimer FL (Fig. 2b). The aggregated pyrene units of the **Q-clip** resulted in the stronger CT interaction with the **NDI** guests,²¹ as the added **NDI** quenches the FL of the **Q-clip** more effectively than compound **1** (Fig. 2c). The unique features of the **Q-clip** as an adaptive molecular clip and **NDI** as an allosteric effector in bulk self-organization were further characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Unlike most of the host molecules that are crystalline,^{24,25} the **Q-clip** is an amorphous liquid as evident from the amorphous halos in the XRD pattern and the lack of endothermic transition in the DSC thermograph (green lines in Fig. 3). On the other hand, the **NDI** guest is a crystalline solid that gives multiple diffraction peaks and endothermic transitions in XRD and DSC measurements (red lines in Fig. 3). As for

the **Q-clip** : **NDI** mixtures, the presence of **NDI** triggers the host-guest assembly. The 1 : 4 **Q-clip** : **NDI** mixture gave three diffraction peaks at $2\theta = 3.4^\circ$, 6.8° , and 10.4° , indicating that each **Q-clip** pinches 4 equivalents (eq.) of the **NDI** guest to self-organize into a lamellar structure with a lamellar spacing (d_{lamellae}) of 26 Å. Moreover, the diffraction peak at $2\theta = 26^\circ$ indicates that the pyrene capture units and the **NDI** guests form orderly packed CT complexes with a π - π stacking distance ($d_{\pi-\pi}$) of 3.4 Å.²¹

The supramolecular structure of the **Q-clip** : **NDI**₄ complexes is illustrated in Fig. 4. The characterization data indicate that the amorphous **Q-clip** has to adapt to 4 eq. of **NDI** guests and use the **pyrene** : **NDI** CT interaction as the driving force to self-assemble in the bulk state. Goodby *et al.* showed that octa-substituted POSS derivatives modified with liquid crystalline (LC) mesogens can self-organize into LC phases.^{26,27} In the smectic LC phases, the octa-substituted POSS derivatives take a rod-conformation and align the long-axes of the rod conformers to form lamellar structures with long-range molecular orientation order. The amorphous **Q-clip** is different from these LC POSS derivatives because it must adapt to the **NDI** guests to self-organize into the lamellar structure. The conformational isomerization of the **Q-clip** involves 4 **NDI** guest molecules pinched by the eight pyrene capture units. This unique adaptive host-guest assembly thus renders the **Q-clip** the first example of the adaptive UMC that self-organizes in the bulk phase. Noteworthy, mixing 4 eq. of pyrene with the **Q-clip** did not activate the adaptive assembly since the amorphous halo of the **Q-clip** can still be found in the XRD pattern of the **Q-clip** : **pyrene** mixture (Fig. S12†). Thus, the adaptive assembly of the **Q-clip** requires the **NDI** : **pyrene** CT interaction rather than the **pyrene** : **pyrene** π - π interaction to activate.

The second unique feature of the **Q-clip** : **NDI** complex is regarding the allosteric effect of the **NDI** guest. In Fig. 3a, it was found that 4 eq. of **NDI** consumed almost all the **Q-clip** in the host-guest assembly, while 2 eq. of **NDI** resulted in a very similar diffraction pattern with a residual amorphous **Q-clip**. The result suggests that even 2 eq. of **NDI** promoted the formation of the **Q-clip** : **NDI**₄ complex rather than other supramolecular entities. Thus, the **Q-clip** is an exclusive unimolecular quaternary clip, which either adapts to 4 **NDI** guests or

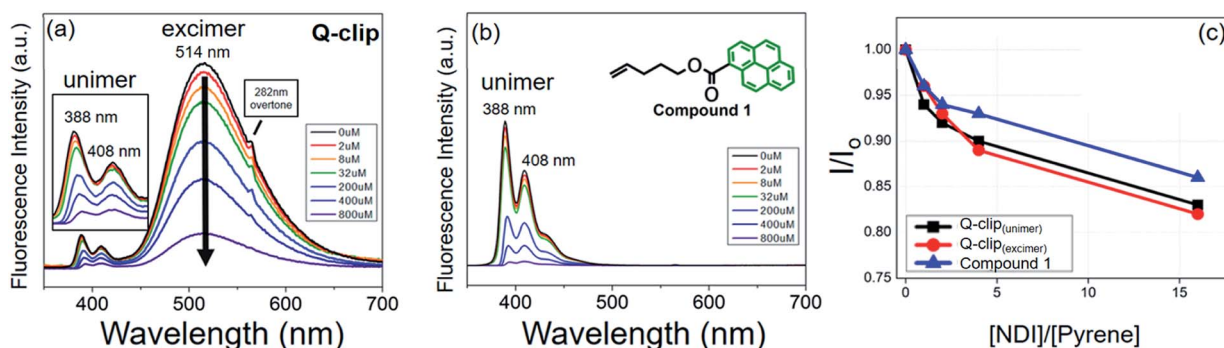


Fig. 2 Fluorescence emission spectra ($\lambda_{\text{ex}} = 282$ nm) of the (a) **Q-clip** (2 μM) and (b) compound **1** (16 μM) in the presence of increasing concentration of **NDI** in CH_2Cl_2 . (c) Fluorescence intensity of the pyrene units as a function of $[\text{NDI}]/[\text{pyrene}]$ in CH_2Cl_2 .

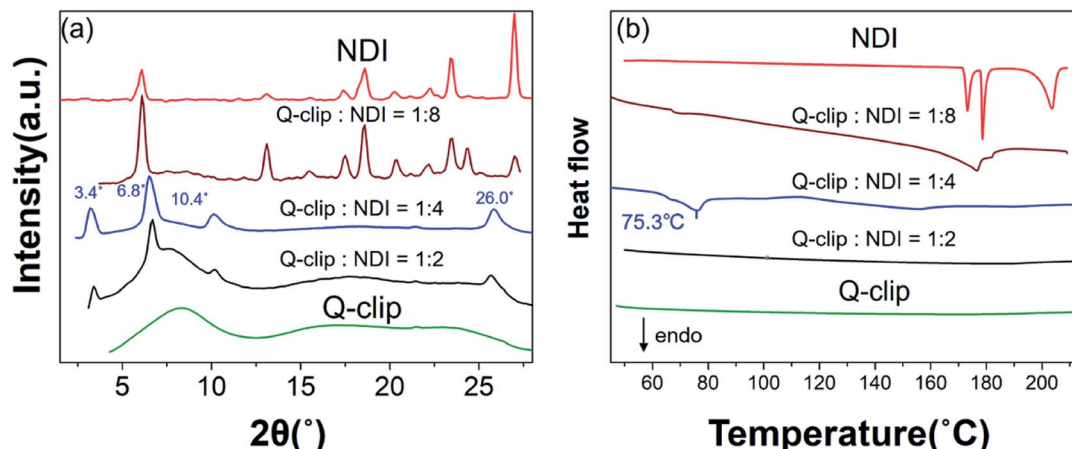


Fig. 3 (a) The XRD patterns of the Q-clip, NDI, and Q-clip : NDI mixtures. (b) The DSC thermograms of the Q-clip, NDI, and Q-clip : NDI mixtures in the heating course.

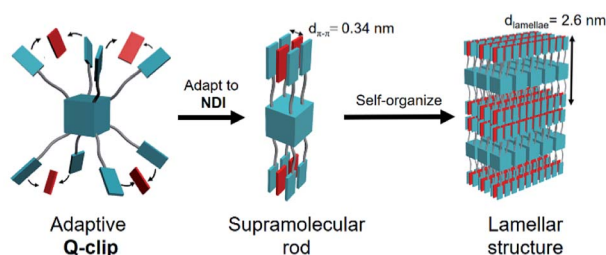


Fig. 4 The illustration of the adaptive host-guest assembly of the Q-clip and 4 eq. of NDI guests in the bulk phase.

not at all, and NDI is an allosteric activator that prevents all self-organization pathways other than the formation of the Q-clip : NDI₄ complex.

Finally, the excess eq. of NDI in the Q-clip : NDI mixture prevents the formation of the Q-clip : NDI₄ complex. In Fig. 3a, the XRD pattern of the 1 : 8 Q-clip : NDI mixture (brown line) contains the diffraction peaks of NDI and the amorphous halos of the Q-clip. No characteristic peak of the Q-clip : NDI₄ complex was detected. In addition, in Fig. 3b, the endothermic phase transition of the supramolecular entity at 75.3°C is also gone. The results indicate that the excess amount of NDI promotes the crystallization of the NDI guest and suppresses the host-guest assembly completely. The distinct morphologies of the 1 : 4 and 1 : 8 mixtures thus indicate that the crystallization of NDI and the host-guest assembly of the Q-clip : NDI mixture are two competitive routes that lead to different ordered phases whose stability depends on the Q-clip : NDI ratio.

Additional features regarding the adaptive assembly were observed in *in situ* POM micrographs shown in Fig. 5. Via supplying the allosteric activators (NDI solution) from the tip of the tissue, the amorphous Q-clip quickly assembled with NDI and formed the birefringent area of the Q-clip : NDI₄ complex within 20 seconds. The fast adaptive assembly allows us to locate the assembly area on the amorphous Q-clip film. When the allosteric activators were supplied from the top of the Q-clip

film via a thin glass capillary, the selective-area growth of the Q-clip : NDI₄ complexes resulted in the birefringent area in Fig. 5d, and left the untreated area dark. Since the assembly area can be determined by where the allosteric activator is applied, the Q-clip may have the potential to be used as a functional material in micro-/nano-fabrications, where the patterns of the Q-clip : NDI₄ complex can be created by micro-/nano-stamps.^{28,29}

In summary, a Q-clip that carries out the adaptive host-guest assembly in the bulk phase was developed. The Q-clip is an eight-arm-star giant molecule consisting of a POSS core and 8 pyrene capture units. It is intrinsically amorphous due to its high conformational freedom but can pinch exclusively 4 eq. of the allosteric activator, NDI, to form the Q-clip : NDI₄ host-guest complex in the bulk phase. In the host-guest complex, the pyrene capture units of the Q-clip and the NDI guests use CT

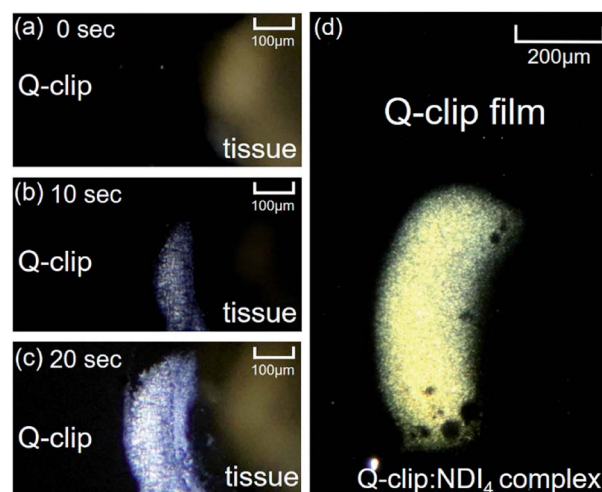


Fig. 5 *In situ* POM images documenting the adaptive assembly of the Q-clip : NDI₄ complex after addition of the saturated toluene solution of NDI from the tip of the tissue at (a) 0 s, (b) 10 s, and (c) 20 s. (d) The quick adaptive assembly of the Q-clip and NDI in the bulk phase.



interactions to form continuous π -stacking, which reduces the conformational freedom of the host and assists the amorphous **Q-clip** to pack into a supramolecular lamellar structure. Increasing the number of binding sites of a host molecule is an important step to evolve host molecules toward complex structures.⁷ Our study breaks the limits on the number of clips in a UMC and overcomes the obstacles posed by the increased molecular complexity. Moreover, the rapid adaptive assembly of the **Q-clip** and **NDI** in the bulk phase allows us to locate the area of the **Q-clip** : **NDI**₄ complexes on the **Q-clip** film and provides the potential for the supramolecular complex to be used as a functional material in micro-/nano-fabrications. These results provide new insights into the design of adaptive UMCs for the development toward complex matters and supramolecular functional materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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