Hierarchical living assembly: fabrication and visualization of multiblock microstructures

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Abstract:

Nature possesses a powerful ability to assemble multiple complex structures to fabricate hierarchical biological structures in a living-assembled way. However, it is still a huge challenge for artificial systems to fabricate and characterize hierarchical living assemblies with well-defined and controllable but complex structures. In this work, we proposed a new concept for the fabrication of multiblock fluorescent microcolumns, which relies on the cooperation between the controllable host–guest complexation based on cucurbit[8]uril (CB[8]) and the living assembly of nanotubular supramolecular polymers composed of CB[8] and NaBr in aqueous solution. By using the complexation of CB[8] with different guest numbers of luminogens with aggregation-induced emission (AIEgens) characteristics, and the difference in affinity between CB[8] and different types of AIEgens, the concentration-controlled and self-sorting-controlled sequential living assembly are realized, respectively. Correspondingly, multiblock fluorescent microcolumns with different fluorescence emission are fabricated, and the molecular structure of each fluorescent block is analyzed by single crystal X-ray diffraction measurement. In addition, the living assembly of multiblock fluorescent microcolumns is visualized, understood, and regulated with the aid of AIEgens. The method developed here is expected to be

extended to more guest molecules of CB[8] and also provides a referential crystallization method for CB[8]-based complexes.

1. Introduction

In biological systems, thousands of molecular building blocks assemble into hierarchical structures, such as actin filaments, microtubules, amyloid fibrils, muscle fibers, *etc.*, through living assembly to carry out sophisticated biological processes.¹ In muscle fiber cells, actin and myosin are actively assembled to form nanoscale multiband—alternating thin and thick filaments, which reassemble to form micron-scale filamentous myofibrils. Then, bundles of muscle fibers are arranged to form centimeter-scale skeletal muscle tissue.² Taking inspirations from nature, it is a very attractive scientific proposition to understand and develop biomimetic artificial hierarchical living assembly.

Indeed, great efforts have been made in the field of living assembly with the ability of epitaxial growth. It is widely known that living polymerization can retain chain-end fidelity, and it thus plays a vital role in the preparation of block copolymers.³⁻⁹ However, the construction of highly complex ordered structures remains a challenge for covalent polymerization, but can be achieved by supramolecular polymer chemistry.¹⁰ In recent years, living supramolecular assembly, such as living supramolecular polymerizations relying on π -stacking molecular amphiphiles, hydrogen bonding, metallophilic interactions, large dipole moment or β -sheet formation,¹¹⁻²⁶ and living crystallization-driven self-assembly of block copolymers,²⁷⁻³¹ have been used to fabricate a variety of

ordered hierarchical assembly structures with remarkable complexity, like block fibers, block nanotubes, multiblock nanowires, 2D platelet co-micelles, *etc.* However, the supramolecular building units have complex structures that may not be well-defined or contain expensive noble metals, and most assemblies are only nanometer to submicron in width. Besides, the variety of living supramolecular assembly is still limited and much work remains to be done. The main reason is that the bottom-up controllable fabrication of living assembly materials with well-defined but complex structures presents a great challenge not only in fabrication but also in structural characterization.

In the past decades, supramolecular polymers have been extensively studied to facilitate its mechanistic interpretation at the molecular level.^{1,20,21,32-48} However, many well-established characterization methods for conventional polymers, such as gel permeation chromatography, mass spectrometry and so on, do not work well because the dilution effect and the detrimental interactions with matrixes may affect the structures of supramolecular polymers due to their dynamic nature.^{45,49} Commonly used spectroscopic techniques such as nuclear magnetic resonance, infrared, and Raman spectroscopy are limited in that they provide an ensemble average information on the molecular interactions, and cannot distinguish subtle variations at the microscopic scale.⁵⁰ Scanning electron microscope, transmission electron microscope and atomic force microscope are also frequently applied, but the first two methods are not suitable for real-time monitoring of the assembly process, or even encounter sample change or damage during sample preparation, while the last method requires a long acquisition time.^{49,51} In addition, it is not easy to grow micron-scale single crystals of

supramolecular polymers that can be used for single crystal X-ray diffraction measurements.⁵² The difficulties of characterizing supramolecular polymer assembly make it difficult for people to understand the assembly mechanism and to achieve in-depth and comprehensive control on the final assembly structures.

Is there any economical and practical characterization method that can visualize the supramolecular assembly process in situ and in real time, and provide real images and reliable results without additional sample preparation process? Fluorescence-based technologies can meet all the above requirements.^{22,53-58} In the study of living supramolecular assembly, traditional fluorescent materials show inherent dilemma: their fluorescence is very bright in solution but is partially or completely quenched upon assembly and aggregation. Such a phenomenon is called aggregation-caused quenching (ACQ).⁵⁹⁻⁶¹ On the contrary, the more materials with the characteristics of aggregation-induced emission (AIE) are assembled, the higher is their emission. Thus, AIE materials can reduce the fluorescence signal in solution but enhance it after assembly,⁶²⁻⁷⁴ making it an inherently promising tool for studying living supramolecular assembly. Our previous work found that AIEgen is not only a versatile probe for visualizing supramolecular assembly, but also an excellent guest for CB[8].⁷⁵ However, we acquired no large ordered assemblies so that we spent great efforts to infer the molecular structures of the supramolecular polymers through various solution characterization methods. We assume that the supramolecular polymer assembly based only on the host-guest interaction of CB[8] and AIEgen is so weak that prevents the further development of assembly. Thus, we hypothesize that large hierarchical structures are expected to

form if multiple supramolecular interactions are used for assembly.

In this work, we aim to develop large and stable supramolecular assembly. According to the literature reports, we noted that CB[6] can form rod-shaped bulk crystals in NaCl solution through various supramolecular interactions.⁷⁶ However, the cavity of CB[6] is too small to accommodate six-membered aromatic ring.⁷⁷ Due to the large cavity size of CB[8], it can accommodate one or two six-membered aromatic rings and shows high binding affinity.⁷⁸⁻⁸¹ We believe that if the host–guest interaction of CB[8] and AIEgen is further combined with the supramolecular interactions of CB[8] and salt,^{82,83} stable hierarchical supramolecular assembly from the molecular level to the nanometer level and then to the micron level may be obtained. Meanwhile, the fluorescence of AIEgens allows us to visualize the assembly process to gain reliable and useful assembly information. In this study, with the aid of AIEgens, we visualized the hierarchical assembly, understood the assembly mechanism, and realized the regulation of supramolecular assembly. This enables us to develop hierarchical living assembly for the fabrication of nano/micro multiblock microstructures in aqueous solution.

2. Results and discussion

2.1. Microcolumns assembled from CB[8] and NaBr in the absence or presence of AIEgens

Since CB[8] shows a symmetrical structure with electrostatically negative carbonyl-fringed portal and electrostatically positive periphery (**Fig. 1a**), it is possible

to form mesoscopic or even macroscopic crystals if the AIEgen-accommodated CB[8] complexes are connected in both the transverse and longitudinal direction through hierarchical supramolecular interactions. We initially checked the crystal assembly of CB[8] and NaCl in aqueous solution by using AIEgen, called CSPP, as a tracer. However, no large assembly was formed in solution (**Supporting Fig. 1**). It is possibly because the radius of Cl^- ion is too small to match the lateral curvature of CB[8]. Therefore, we further tried NaBr and NaI, and found that assembly of CB[8] and salt is easier to form as the radius of halogen anion is much larger (**Supporting Fig. 1**). However, the assembly of NaI and CB[8] grows too fast, which is not conducive to the regulation and real-time monitoring of assembly. Therefore, NaBr is a better choice among NaCl and NaI.

Figure 1 | Microcolumns assembled from CB[8] and NaBr in the absence or presence of AIEgens. **a**, Chemical structure and electrostatic potential (EP) maps of CB[8]. **b**, Bright field (BF) and fluorescence (FL) images of a microcolumn assembled from CB[8] and NaBr. The microcolumn is non-emissive and is thus framed with dotted

line for clarity. λ_{ex} : 400–440 nm; scale bar: 20 μm . **c,d**, Top (**c**) and side (**d**) views of the X-ray single crystal structure of the microcolumn. Nanocavities in the microcolumns are depicted in greenish blue bars. **e,f**, Simplified illustrations of the supramolecular interactions (**e**) between Na^+ cations and the portal of CB[8] in epitaxial direction, and (**f**) between Br^- anions and the periphery of CB[8] in lateral direction. **g**, Chemical structure of CSPP (an AIEgen) and BF and FL images of the microcolumn assembled from CSPP, CB[8] and NaBr. λ_{ex} : 400–440 nm; scale bar: 20 μm . **h**, X-ray single crystal structure of the red-emissive microcolumn. CSPP dimers are incorporated into the CB[8]– Na^+ cation nanotubular polymer via supramolecular host–guest complexation.

NaBr is assembled with CB[8] to form colorless and non-emissive column-like crystals as shown in **Fig. 1b**. The X-ray single crystal analysis shows that the nanochannels are axially distributed in the non-occupied column composed of NaBr and CB[8] (**Fig. 1c** and **1d**). In axial direction, the symmetric coordination interactions of Na^+ cation and the carbonyl oxygen of CB[8] portal axially connect the supramolecular assembly to form nanotube through $[\text{O}_{\text{carbonyl}}-\text{Na}-\text{O}_{\text{carbonyl}}]$ coordination interactions at distances of 2.337(8), 2.367(8), 2.368(8) and 2.406(7) Å (**Fig. 1e**). Eight Na^+ cations are located above the eight carbonyl oxygens of CB[8] portal to form a circle. The Na^+ cations are also linked by structural water through $[\text{Na}-\text{O}_{\text{water}}]$ coordination interactions to enhance the stability of the nanotube at a distance range of 2.00(3)–2.57(4) Å. Since the nanotubes formed by CB[8] and Na^+ cations are straight and rigid, they are suitable for further lateral association with each other.⁸⁴ Laterally, the Br^- anions interact with the periphery of CB[8] through the $[\text{Br}\cdots\text{C}=\text{O}]$ ion–dipole interactions with the electrostatically positive carbonyl carbon atoms of

CB[8], and also through the special [Br $\cdots$ H–C] hydrogen bonding with the methine and methylene groups of CB[8]. The distances of these interactions fall in the range of 3.37(1)–3.697(8) Å and 3.11–3.45 Å, respectively. At the same time, the Br $^-$ anions also interact with structural waters through [Br $\cdots$ H–O] hydrogen bonds at a distance range of 2.38–2.95 Å. Thus, these ion–dipole interactions and hydrogen-bonding interactions connect one CB[8] in the center with surrounding six CB[8]s to serve as a repeating unit of the assembly, which connect the nanotubes together to form multi-stranded tubules (**Fig. 1f**). Detailed crystal information can be found in **Supporting Fig. 2** and **Supporting Table 2**.

CSPP molecule has a rotatable donor–acceptor structure, and shows a remarkable effect of twisted intramolecular charge transfer. As the polarity of the surrounding environment decreases, its emission is red-shifted from 524 nm to 644 nm (**Supporting Fig. 3**). Therefore, CSPP is expected to be used for sensitive tracking and functionalizing supramolecular assembly. After CSPP was mixed with CB[8] and NaBr, red-emissive brownish-colored fluorescent microcolumns were observed by fluorescence imaging (**Fig. 1g**). Analysis of its single crystal structure by X-ray diffraction measurement reveals that CSPP dimers are distributed in the nanotube formed by CB[8] and Na $^+$ cations (**Fig. 1h**). The dimers have two conformations that can be transformed to each other by flipping horizontally. The distance between the centers of two parallel benzene rings in the dimer is 3.4943(1) Å, indicating the existence of a strong π – π interaction. The enhancement of conjugation between CSPP molecules in the dimer promotes fluorescence redshift. In addition, the guest molecule

in the nanotube strengthens the axial connection of CB[8]s through the ion–dipole interaction of its positively charged nitrogen and the carbonyl oxygen of CB[8], thereby improving the stability of CSPP dimer@CB[8]–NaBr crystals. This explains why CSPP dimer@CB[8]–NaBr crystals can be formed at lower concentrations than CB[8]–NaBr crystals. In nanotubes, there are 8 Na⁺ cations located above each CB[8] portal in most cases, while there are only 4 Na⁺ cations located above CB[8] portal at the position of two parallel benzene rings (**Fig. 1h**). Perhaps it is because the two parallel benzene rings occupy too much space, there is not enough space to accommodate more Na⁺ cations. And the carbonyl oxygens of CB[8] portal that are not combined with Na⁺ cations form hydrogen bonds with structural water to enhance the stability of the nanotubes (**Supporting Fig. 4**). Like CB[8]–NaBr crystal, the adjacent nanotubes in CSPP dimer@CB[8]–NaBr crystal are connected by [Br[−]⋯C=O] ion–dipole interactions and [Br[−]⋯H–C] hydrogen bonds of Br[−] anions with the periphery of CB[8], and the [Br[−]⋯H–O] hydrogen bonds of Br[−] anions with structural water (**Supporting Fig. 4 and Supporting Table 3**). Therefore, the axial and lateral connections inside the column and the encapsulating capability of CB[8] cavities indicate the nature of hierarchical assembly.

2.2. Fabrication of triblock fluorescent microcolumns

Since both the non-emissive (N) column and the red-emissive (R) column contain the framework composed of CB[8] and NaBr, we assumed that N and R can form a block structure under certain conditions. If CB[8] is in excess, it may continue to grow at both ends of the already formed R to form a N–R–N triblock column. After

optimizing the fabrication conditions, colorless–brownish–colorless triblock columns form and are observed in the bright field images (**Fig. 2a** and **2b**), indicating that the system is living assembly. Interestingly, by controlling the relative concentration of CB[8] to AIEgens and the evaporation rate, two types of triblock fluorescent columns, namely the N column at the end of R (N–R–N) and the yellow-emissive column at the end of R (Y–R–Y) are found (**Fig. 2a** and **2b**). Although they show similar bright field images, their fluorescence images are completely different. Compared with the preparation conditions of N–R–N triblock, Y–R–Y triblock fluorescent column is produced under the condition of reduced concentration of CB[8] and fast solution evaporation.

Figure 2 | Fabrication of 3-block fluorescent microcolumns through optimization of conditions. **a,b**, BF and FL images of (a) N–R–N and (b) Y–R–Y triblock microcolumns made from CB[8], NaBr and CSPP. R = red-emissive block, Y = yellow-emissive block, N = non-emissive block. The fluorescent microcolumn in the right panel of **a** is framed with white dotted line for clarity; λ_{ex} : 400–440 nm. **c**, X-ray single crystal structure of the Y block. CSPP monomers are incorporated into the CB[8]–Na⁺

cation nanotubular polymer via host–guest complexation. **d**, FL spectra of the R and Y blocks shown in the right panel of **b** measured by a home-built optical system; λ_{ex} : 415 nm.

It is well-known that the nanoconfined space of artificial macrocycles can make the encapsulated guest molecules to adopt a specific conformation, intermolecular distance or packing style.^{42,81,85-88} This may be the cause of the change in the emission behavior of AIEgens in CB[8] macrocycles. To figure out the molecular structure of the Y block, we obtained and studied its single crystal structure. X-ray diffraction analysis reveals that the crystal also shows a framework composed of CB[8] and NaBr (**Supporting Fig. 5**). The CSPP molecules are distributed in CB[8]–Na⁺ cation nanotubes in the form of monomer. There are four conformations of CSPP monomer, which can be converted to each other by vertical +/- horizontal flipping. Two of them are shown in **Fig. 2c**, and the rest are shown in **Supporting Fig. 6**. In the Y–R–Y triblock fluorescent column as shown in **Fig. 2b**, the fluorescence emission maximum of Y is located at 570 nm, while that of R is 650 nm (**Fig. 2d**). The different emission of Y and R can be explained by using theoretical calculation on the frontier molecular orbitals and the potential energy surface as shown in **Supporting Fig. 7** and **Supporting Fig. 8**. It is revealed that the energy gap between the HOMO and LUMO of CSPP monomer@CB[8] is higher than that of CSPP dimer@CB[8] (**Supporting Fig. 7**). This is mainly because the torsion angle of CSPP monomer in the hydrophobic CB[8] cavity is close to right angle (-96.59°), which results in a high potential energy surface and blue-shifted emission. However, the torsion angle of CSPP dimer in CB[8] cavity

is very small (-1.04°), which leads to a small potential energy surface (**Supporting Fig. 8**). Together with its enhanced π - π conjugation, CSPP dimer@CB[8] shows a red-shifted emission.

In addition, the formation mechanism of Y-R-Y and N-R-N triblock fluorescent columns was analyzed. The sequential living assembly process of Y-R-Y triblock was monitored and demonstrated by fluorescence imaging (**Supporting Fig. 9**). In solution, the CB[8] cavity of CSPP monomer@CB[8] contains more high-energy water, resulting in its structural instability, while CSPP dimer@CB[8] is relatively more stable and preferentially exists in solution.⁸⁹ Thus, we can conclude that when the CSPP concentration is relatively high, the CSPP dimer@CB[8]-NaBr polymers are predominant in solution. On the other hand, when CB[8] is in excess, the CSPP monomer@CB[8]-NaBr and CB[8]-NaBr polymers preferentially exist in solution after the consumption of most CSPP to produce R. And after the solution evaporation to reach the saturation of CB[8], both can be assembled and fixed. By using PL and UV-vis spectroscopy to track the change of the solution that is similar to the residual solution after the formation of R upon gradual addition of CB[8], the assembly process of CSPP monomer@CB[8]-NaBr and CB[8]-NaBr polymers was demonstrated (**Supporting Fig. 11**). It is worth noting that the CSPP dimer@CB[8]-NaBr polymer and the CSPP monomer@CB[8]-NaBr polymer can be interconverted to each other under certain conditions, and such transformations were directly visualized and tracked through real-time fluorescence imaging as shown in **Supporting Fig. 13**, but failed to be observed by bright field imaging and electron microscopic imaging. To fabricate Y-

R–Y triblock, the solution was evaporated rapidly. In this case, CSPP monomer@CB[8]–NaBr polymers do not have sufficient time to transform into CSPP dimer@CB[8]–NaBr polymers. When CB[8] reaches saturation, they epitaxially grow at both ends of R to form Y–R–Y triblock. For the fabrication of N–R–N triblock, the solution was evaporated more slowly. Therefore, in the presence of more CB[8] and under the condition of slow solution evaporation, the CSPP monomer@CB[8]–NaBr polymers have enough time to transform into the thermodynamically more stable CSPP dimer@CB[8]–NaBr polymers, whose assembly makes the R column continue to grow, eventually leading to the complete consumption of CSPP. Subsequently, the excess CB[8] continues to be epitaxially assembled with NaBr at both ends of R to generate N–R–N triblock.

Therefore, the formation of N–R–N and Y–R–Y triblock is mainly affected by the relative concentration of CB[8] and the evaporation rate of solution. Considering that the one-pot assembly of fluorescent multiblock columns is a concentration-controlled sequential living assembly process, it is probably affected by the CB[8] concentration, the relative ratio of guest to CB[8], the guest concentration, the NaBr concentration, and the evaporation rate of solution. Adjustment of these factors is expected to produce more complex assemblies.

2.3. One-pot multiblock living assembly

Nature always uses multiple components to build hierarchical complex biological assemblies. By drawing inspiration from nature, we hope to use N, R, and Y columns as building blocks to create more complex structures through the one-pot living

assembly as now we know the conditions under which they are formed. Taking the formation conditions of N–R–N triblock (3-block) into account, we slightly increased the relative ratio of AIEgen to CB[8] while keeping the amount of CB[8] in excess, and also speed up the evaporation process. When CB[8] reaches saturation after R is formed, the CB[8]–NaBr polymers continue to grow at the R terminals to form N. With the consumption of CB[8], the concentration of CSPP monomer@CB[8]–NaBr polymers increases relatively, and their continued growth at the end of N–R–N leads to form the penta-block (5-block) fluorescent microcolumn Y–N–R–N–Y (**Fig. 3a**). In addition, based on the formation conditions of Y–N–R–N–Y 5-block, we increased the concentration of CB[8]. Therefore, after Y–N–R–N–Y 5-block is generated, there is still residual CB[8] in the system, which continues to grow N at the terminals of Y–N–R–N–Y to lead to the formation of hepta-block (7-block) fluorescent microcolumn N–Y–N–R–N–Y–N (**Fig. 3b**).

Figure 3 | Fabrication of 5-block and 7-block fluorescent microcolumns through one-pot living assembly. FL and BF images of the microcolumns with (a) Y–N–R–N–Y and (c) N–Y–R–Y–N penta-block and (b) N–Y–N–R–N–Y–N and (d) Y–N–Y–R–Y–N–Y hepta-block. λ_{ex} : 400–440 nm. The fluorescent microcolumns are framed with white dotted lines for clarity. R = red-emissive block, Y = yellow-emissive block, N = non-emissive block.

In addition, on the basis of the formation condition of Y–R–Y 3-block, we increased the relative ratio of CB[8] to AIEgen. After Y–R–Y is generated, the remaining CB[8]s in the system continue to assemble at the terminals of Y–R–Y to generate N, leading to the formation of N–Y–R–Y–N 5-block fluorescent microcolumns (**Fig. 3c**). Moreover, based on the formation conditions of N–Y–R–Y–

N 5-block, we increased the concentration of AIEgens. After N–Y–R–Y–N is generated, there is still CSPP monomer@CB[8]–NaBr polymers in the system, which continues to grow at the ends of N–Y–R–Y–N to produce Y, thereby forming Y–N–Y–R–Y–N–Y 7-block fluorescent microcolumns (**Fig. 3d**).

2.4. Stepwise sequential multiblock living assembly

Figure 4 | Fabrication of multiblock fluorescent microcolumns through stepwise sequential living assembly. **a**, Schematic illustration of 2-step living assembly to fabricate 3-block fluorescent microcolumns. **b,c**, FL and BF images of **(b)** R seeds and **(c)** Y–R–Y 3-block microcolumns formed after addition of the growth solution and slow evaporation. **d**, Schematic illustration of 2-step living assembly to fabricate 5-block fluorescent microcolumns. **e,f**, FL and BF images of **(e)** R seeds and **(f)** N–Y–R–Y–N 5-block microcolumns formed after addition of the growth solution and slow evaporation. λ_{ex} : 400–440 nm. The fluorescent microcolumns are framed with white dotted lines for clarity. R = red-emissive block, Y = yellow-emissive block, N = non-emissive block.

Stepwise assembly by adding dormant building blocks in sequence is a widely used method to prepare supramolecular block copolymers, multiblock fibers or

multiblock fluorescent rods after a nucleation-elongation growth process.⁹⁰⁻⁹² Now we have successfully fabricated 3-block, 5-block and 7-block fluorescent microcolumns through one-pot living assembly, we also want to fabricate multiblock fluorescent microcolumns through conventional stepwise living assembly as to prove the versatility of this assembly system.

In the first step, R seeds are prepared after evaporating the solution. Then, an appropriate amount of growth solution is added to R seeds, as illustrated in the schemes of **Fig. 4a** and **4d**. The growth solution contains low concentration of CSPP, excessive CB[8] and a high concentration of NaBr. After adding the growth solution, the system mainly contains the building units of CSPP monomer@CB[8]–NaBr polymers and CB[8]–NaBr polymers for living assembly. The formed R seeds are shown in **Fig. 4b** and **4e**. After adding the growth solution to the R seeds, the mixture was evaporated. In the presence of a slight excess of CB[8] and under the condition of rapid evaporation, the CSPP monomer@CB[8]–NaBr polymers epitaxially grow at the ends of R to form Y–R–Y 3-blocks (**Fig. 4c**). For the fabrication of N–Y–R–Y–N 5-block microcolumns, a growth solution was added to the R seeds, and the mixture was evaporated. Under the conditions of excessive CB[8] and rapid solution evaporation, Y columns are first formed at the ends of R until all the CSPP monomer@CB[8]–NaBr polymers are completely consumed. Then, the excessive CB[8] continues to assemble epitaxially at the ends of Y–R–Y to generate N–Y–R–Y–N 5-blocks (**Fig. 4f**).

2.5. One-pot sequential self-sorting multiblock living assembly from different types of AIEgen guests

Since CB[8] has a variety of guest types,^{33,78,93} CB[8]–NaBr polymers may serve as a framework to accommodate other guests to form microcolumns with different fluorescence emission. Because of the difference in affinity between different guests and CB[8], it is possible to fabricate multiblock fluorescent microcolumns through supramolecular self-sorting-controlled sequential multiblock living assembly. To prove this concept, we chose another type of AIEgen, called CSPyP, whose structure is like CSPP but possesses pyridine instead of pyridinium group (**Fig. 5a**). As we expected, CSPyP can assemble with CB[8] and NaBr to form microcolumns (**Fig. 5a**) with green emission (G) at 558 nm (**Supporting Fig. 14**). Analysis of its single crystal structure by X-ray diffraction measurement (**Supporting Fig. 15**) found that CSPyP dimers are distributed in CB[8]–Na⁺ cation nanotubes probably in the form of AA, BB and AB packings (**Fig. 5b**). In addition to ion–dipole interactions and hydrophobic interactions with CB[8], CSPyP also shows strong C–H··· π interactions in the dimers of AA and AB packings (**Supporting Fig. 16**).

Figure 5 | One-pot sequential self-sorting multiblock living assembly from different types of AIEgen guests. **a**, Chemical structure of CSPyP and FL and BF images of green-emissive microcolumns assembled from CB[8], NaBr and CSPyP; λ_{ex} : 400–440 nm. **b**, X-ray single crystal structure of the green-emissive microcolumn. **c**,

Schematic illustration of one-pot fabrication of G–R–G 3-block fluorescent microcolumns from a mixture of CSPP, CSPyP, CB[8] and NaBr. G = green-emissive block, R = red-emissive block. **d**, FL and BF images of G–R–G 3-block microcolumns; λ_{ex} : 400–440 nm.

Since the portal of CB[n]s is highly electrostatically negative and the inner cavity of CB[n]s is remarkably hydrophobic, CB[n]s show a preference to dicationic species in which the charges are separated by hydrophobic regions.⁷⁷ Because CSPP has two positive charges separated by hydrophobic aromatic groups, the host–guest affinity of CSPP with CB[8] is stronger than that of CSPyP, because it possesses less positive charge than CSPP. Therefore, it is assumed that CSPP dimer@CB[8]–NaBr polymers are first assembled to form R columns. After they are completely consumed, the CSPyP dimer@CB[8]–NaBr polymers will continue to grow epitaxially at the R terminals to generate 3-block columns as illustrated in **Fig. 5c**. To verify the hypothesis, we mixed CSPP and CSPyP at a ratio of 1:1 as the guest. The fluorescence and bright field images of the formed assemblies in **Fig. 5d** indicate that the mixed guests do indeed assemble with CB[8] and NaBr to form G–R–G 3-block fluorescent microcolumns. Therefore, it is proved that the mixture can undergo supramolecular self-sorting to form CSPP dimer@CB[8]–NaBr polymers and CSPyP dimer@CB[8]–NaBr polymers. The former is more stable and can be assembled first, and the latter is assembled at the end of R formed by the former (CSPP dimer@CB[8]–NaBr polymers), thus realizing the self-sorting-controlled sequential multiblock living assembly in one pot.

3. Conclusions

In the present work, the nanotubular supramolecular polymer formed by the supramolecular interactions of CB[8] macrocycle and NaBr is used as the framework, which is axially connected by CB[8] and Na⁺ cations and is further laterally connected by Br⁻ anions to form a large columnar assembly. And its ability of continuous epitaxial growth realizes the living assembly. In addition, the hierarchical living assembly of the multiblock microcolumns composed by CB[8], NaBr and AIEgens in aqueous solution is visualized by the fluorescence properties of AIEgens. By making use of the complexation between CB[8] and different numbers of AIEgen guests (2, 1, 0), the concentration-controlled sequential living assembly is realized to achieve multiblock fluorescent microcolumns with different fluorescence emission, such as Y-R-Y and N-R-N 3-blocks, N-Y-R-Y-N and Y-N-R-N-Y 5-blocks, Y-N-Y-R-Y-N-Y and N-Y-N-R-N-Y-N 7-blocks. In addition, by using the difference in affinity between CB[8] and different types of AIEgen guests, the self-sorting-controlled sequential living assembly is achieved, leading to the fabrication of G-R-G 3-block fluorescent microcolumns. Furthermore, the molecular structure of each fluorescent block is analyzed by single crystal X-ray diffraction measurement.

To our knowledge, the complex multiblock assemblies made by artificial macrocycle and ordinary salt in aqueous solution are unprecedented so far. This method is very simple, and the raw materials are economical and non-toxic. Since CB[8] can accommodate guests of many kinds, our method is expected to be extended to more guest molecules to construct more multiblock microcolumns with different fluorescent

colors, which has a broad application prospect in anti-counterfeiting fluorescent barcode. In addition, due to the importance of single crystals in structural analysis, the preparation of large crystals of supramolecular host–guest complex has always been a difficult task. In this work, the crystallization of the complex of CB[8] and its guest is easily achieved by using the nanotubular supramolecular polymers formed by CB[8] macrocycle and NaBr as a framework. Therefore, our research also provides a referential crystallization method for CB[8]-based complexes.

Accession Codes. CCDC 2034452, 2110796, 2034451 and 2110704 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

This project was financially supported by the National Natural Science Foundation of China Grants (21788102, 82072167, and 81873931), the Innovation and Technology Commission (ITC-CNERC14SC01), the Research Grants Council of Hong Kong (16307020, C6014-20W, and N-HKUST609/19), the Science and Technology Plan of Shenzhen (JCYJ20170818113538482), and the Research and Development program from Hubei Province (2021ACB001).

Author Contributions

X. Shi and J. Zhang contributed equally to this work. Dr. X. Shi did the experiments, analyzed the data, wrote the manuscript, and supported the funding. Prof. J. Zhang gave suggestions for crystal growth and analyzed the raw data of single crystal X-ray diffraction measurements. Dr. J. Liu did the computational calculations. Dr. X. Zhao, Dr. H. Wang and Prof. P. Wei made suggestions for writing the manuscript. Prof. X. Ni provided CB[8]. Dr. Herman H.-Y. Sung and Prof. Ian D. Williams did the single crystal X-ray diffraction measurements. Mr. W. K. Ng and Prof. K. S. Wong measured the fluorescence emission by using a home-built optical system. Dr. Jacky W. Y. Lam revised the manuscript. Prof. L. Wang supported the funding. Prof. B. Z. Tang supported the funding, revised the figures, and conceived the outline of the manuscript.

Competing Interests statement

The authors declare no competing interests.

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