

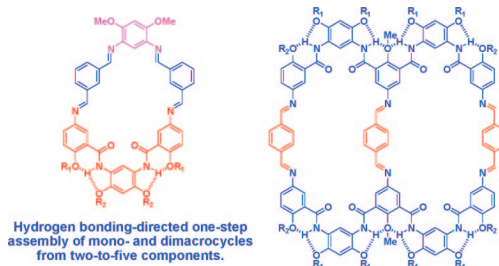
Hydrogen Bonding-Directed Multicomponent Dynamic Covalent Assembly of Mono- and Bimacrocycles. Self-Sorting and Macrocycle Exchange

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This paper describes the multicomponent dynamic covalent assembly of macrocyclic structures by utilizing hydrogen bonding-driven zigzag anthranilamides as “leading” components. Two or three amino groups have been introduced to one side of hydrogen bonded anthranilamide oligomers. The preorganization of the frameworks enabled the amino groups to condense with structurally matched aldehydes to form mono- and bimacrocycles in good to quantitative yields. Reactions from up to five components have been investigated, which involved one-step formation of up to six imine bonds. The preorganization of the templates highly enhanced the stability of the macrocyclic structures. As a result, all the macrocycles could be purified by simply recrystallizing the crude products from suitable solvents. Coexisting experiments of three series of three to five components were also performed, which all revealed that the preorganized precursors possessed high self-sorting capacity. On the basis of the same approach, a hydrazone-based macrocycle was also prepared quantitatively, while an intermacrocycle hydrazone–imine exchange was revealed to facilitate the formation of the hydrazone-based macrocycle from an imine-based macrocycle.

Introduction

Macrocycles of defined shape and size are useful architectures for studies in molecular recognition, sensors, and porous materials.^{1,2} Traditionally, this family of structures has been mainly prepared by making use of kinetically controlled cyclization strategy. This approach is able to allow precise control over monomer composition and sequence selectivity, but generally suffers the competition of more favorable polymerizing reactions. Although the template strategy has been developed,³ frequently macrocyclic structures cannot be generated in acceptable yields. Recent advance in dynamic covalent

chemistry (DCC) has offered a new robust approach.⁴ With this thermodynamically controlled strategy, two- and three-dimensional macrocyclic systems can be quickly constructed from simple and multiple components.^{5–11} In this context, the formation of the imine bond from various aldehyde and amine precursors has been most extensively investigated.^{5–7} Owing to the inherent instability of the imine bond, many imine-related structures could not be purified from the solution and therefore require being reduced to the corresponding amine derivatives.^{6,7} One strategy of overcoming this is to preorganize the precur-

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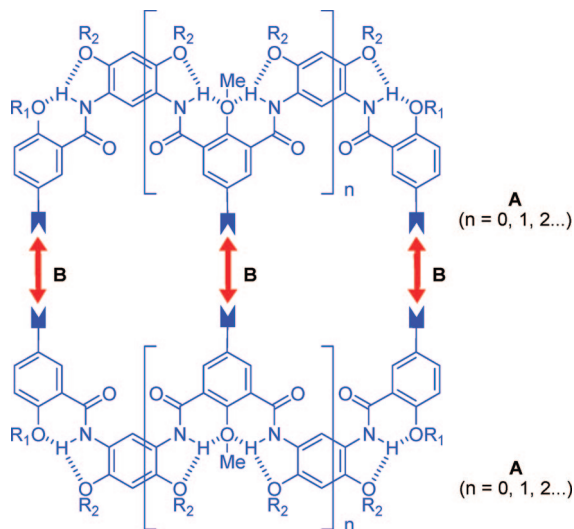


FIGURE 1. Schematic diagram of hydrogen-bonding-driven preorganized oligoanthranilamides (A) as templates for multicomponent dynamic covalent assembly of macrocyclic structures. In principle, the reactive sites may be amino, aldehyde, hydrazine, or any other groups that undergo reversible reactions.

sor(s) to increase the stability of the corresponding macrocycles,^{12,13} as employed in studies in molecular recognition and self-assembly.¹⁴

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In the past decade, foldamers, the linear molecules that are induced by noncovalent forces to adopt compact conformations, have received considerable attention.^{15–17} In particular, three-center hydrogen bonding-driven aromatic amide foldamers usually possess highly predictable secondary structures due to the directionality of hydrogen bonding as well as the inherent rigidity and planarity of aromatic amide units.¹⁶ Recently several preorganized frameworks of this family have been utilized for one-step synthesis of several cyclophanes by directing successive, ordered amide coupling.¹⁸ We previously developed a family of zigzag anthranilamide oligomers, which may be considered as a combination of short folded segments.¹⁹ More recently, we demonstrated that such extended rigid structures are useful frameworks in designing new preorganized supramo-

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lecular synthons or synthetic receptors for guest recognition.²⁰ Herein, we describe that, by using hydrogen bonded preorganized frameworks that carry amino and/or aldehyde groups as “leading” components,²¹ a variety of imine-based mono- and bimacrocycles can be quickly assembled in high to quantitative yields from up to five components. The new macrocycles are all stable and therefore can be purified by simple recrystallization. Coexisting experiments reveal that the precursors also possess high selectivity and fidelity in forming respective macrocycles. In addition, preorganization can also accelerate the formation of a hydrazone-based macrocycle through inter-cycle hydrazone–imine exchange with an imine-based macrocycle.

Results and Discussion

Design and Synthesis. We have previously demonstrated that the framework of aromatic amide oligomers **A** adopts a rigid zigzag conformation.^{19,20b} It occurred to us that iterative introduction of reversible reactive sites, such as amino or aldehyde groups, at the para-positions of the alkoxyl groups of the benzamide and isophthalamide moieties would produce highly preorganized comb-styled structures (**A**, Figure 1). Because all the reactive sites are located at the same side of the backbones, they were expected to template the formation of macrocyclic architectures by reacting with single or multiple structurally matched molecules of complementary reactive sites (**B**, Figure 1). To test this potential, discrete rigid and flexible precursors of varying shape, length, and reactive sites were synthesized. The synthetic details and characterization data are provided in the Supporting Information.

Two-Component Condensation. Dialdehyde **1** and diamine **2** (Scheme 1) were first prepared. Their crystal structures were obtained, which exhibited the expected U-shaped conformations stabilized by two pairs of three-center hydrogen bondings (Figure 2a,b). It can be found that the distances between their respective reactive sites are very close, which boded well for efficient [1+1] condensation. The condensation reaction was first performed in chloroform (Scheme 1). ¹H NMR tracking in CDCl₃ showed that the reaction reached equilibrium within 15 h, with a small amount of precursors unconsumed, to give macrocycle **3** in 75% yield (Figure 3a–c). The macrocycle was found to be stable in solution and solid state and therefore was purified by simply recrystallizing the reaction residue from chloroform and ethanol. In the presence of dry magnesium sulfate or molecular sieve, the yield could be increased notably. This was not unexpected because the reaction was of thermodynamic control with water as one product. Macrocycle **3** was comprehensively characterized by NMR, (HR)MS, and X-ray crystallography (Figure 2c). Because it has been established that

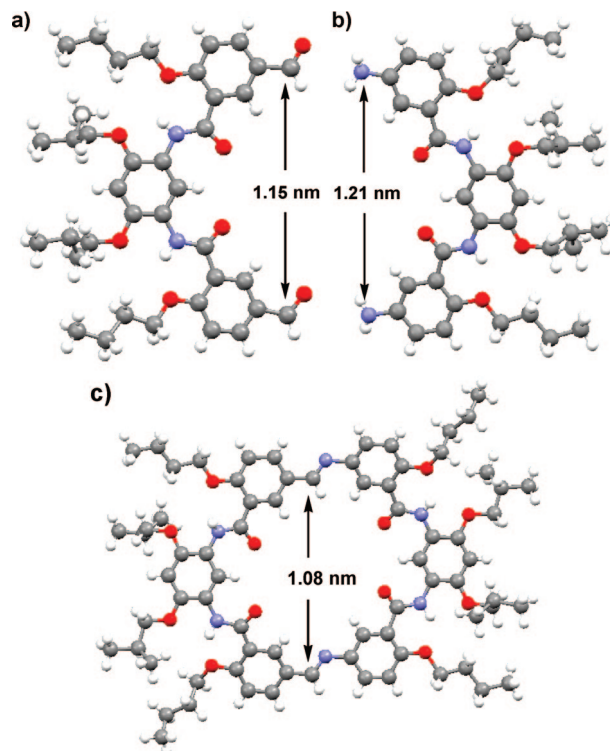
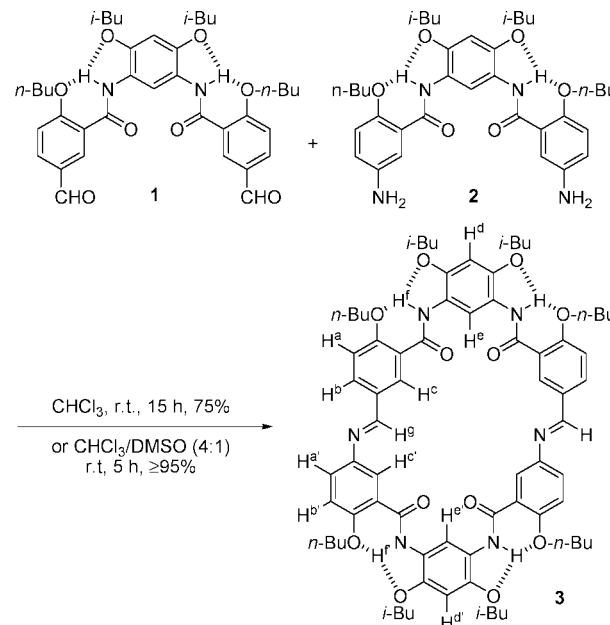


FIGURE 2. Crystal structures of compounds (a) **1**, (b) **2**, and (c) **3**.

SCHEME 1. Synthesis of Macrocycle **3** from [1+1] Condensation Reaction of **1** and **2**



the intermolecular three-center hydrogen bonding survives in polar solvent,²² the reaction was also investigated in a binary solution of chloroform and DMSO (4:1, v/v). Surprisingly, the reaction afforded **3** in shorter time, but the selectivity was increased substantially, as indicated by ¹H NMR (Figure 3d,e), possibly because the larger aggregation capacity of the macrocycle relative to the precursors stabilized the macrocycle, as

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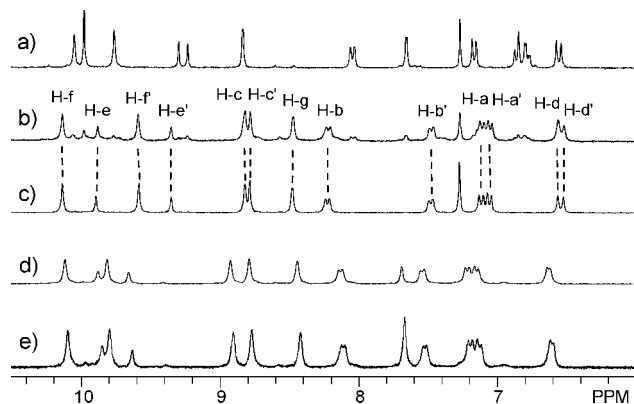


FIGURE 3. Partial ¹H NMR spectra of (a) **1** + **2** (5 min), (b) **1** + **2** (15 h), and (c) **3** in CDCl₃, and (d) **1** + **2** (5 h) and (e) **3** in CDCl₃/DMSO-*d*₆ (4:1) ([**1**] = [**2**] = [**3**] = 2.5 mM, see Scheme 1 for peak marking).

revealed for *m*-phenylene ethynylene-based macrocycles.²³ The distance between the two imine units of **3** in the crystal structure is approximately 1.08 nm, which is very close to those between the reactive sites of precursors **1** and **2**. This result implies that no large tension was produced during the formation of **3** from **1** and **2**. Therefore, the efficiency for the formation of **3** was clearly a result of the highly structural matching of the precursors. In contrast, under the same reaction conditions, no macrocyclic products could be separated from the reaction of **2** with flexible dialdehyde **4**,²⁴ although mass spectrometry indicated that the 1+1 macrocycle was formed from the reaction. The result also illustrates the efficiency of the hydrogen bonding-mediated preorganization of the precursors that not only promoted macrocyclization but also stabilized the macrocyclic product.

Compounds **5**–**7**, which carry both NHBoc and CHO groups, were also prepared for [1+1] condensation studies. This series of precursors possess the same aromatic skeleton, but the number of intramolecular hydrogen bonds is successively decreased. Therefore, the role of the intramolecular hydrogen bonding might be more reasonably revealed from their macrocyclization results. The Boc group was introduced to these precursors because molecules containing both amino and aldehyde units would be difficult to manipulate. Trifluoroacetic acid (TFA, 10 equiv) was used to remove the Boc group and also to catalyze the condensation process. ¹H NMR indicated that the reaction of **5** also selectively afforded [1+1] macrocycle **8** (Figure 4a–f). After the reaction was finished, the solution was washed with aqueous sodium bicarbonate solution and brine and dried over sodium sulfate. Upon removal of the solvent, macrocycle **8** could be obtained for analysis. ¹H NMR tracking also showed that the reaction first gave rise to **8** and other products. The latter, however, were converted into **8** within approximately 1.5 h (Figure 4b–d). Under the same conditions, **6** could also form macrocyclic product (**9**), but in considerably lower yield (65%), while macrocyclic product could not be separated from the reaction mixture of **7**. Mass spectrometry of the reaction mixture of **7** did show the peak of the 1+1 macrocyclic product, which, however, coexisted with Boc-removed **7**, linear dimer, and trimer (see the Supporting Information). These results again illustrate that the intramolecular hydrogen bonding of the

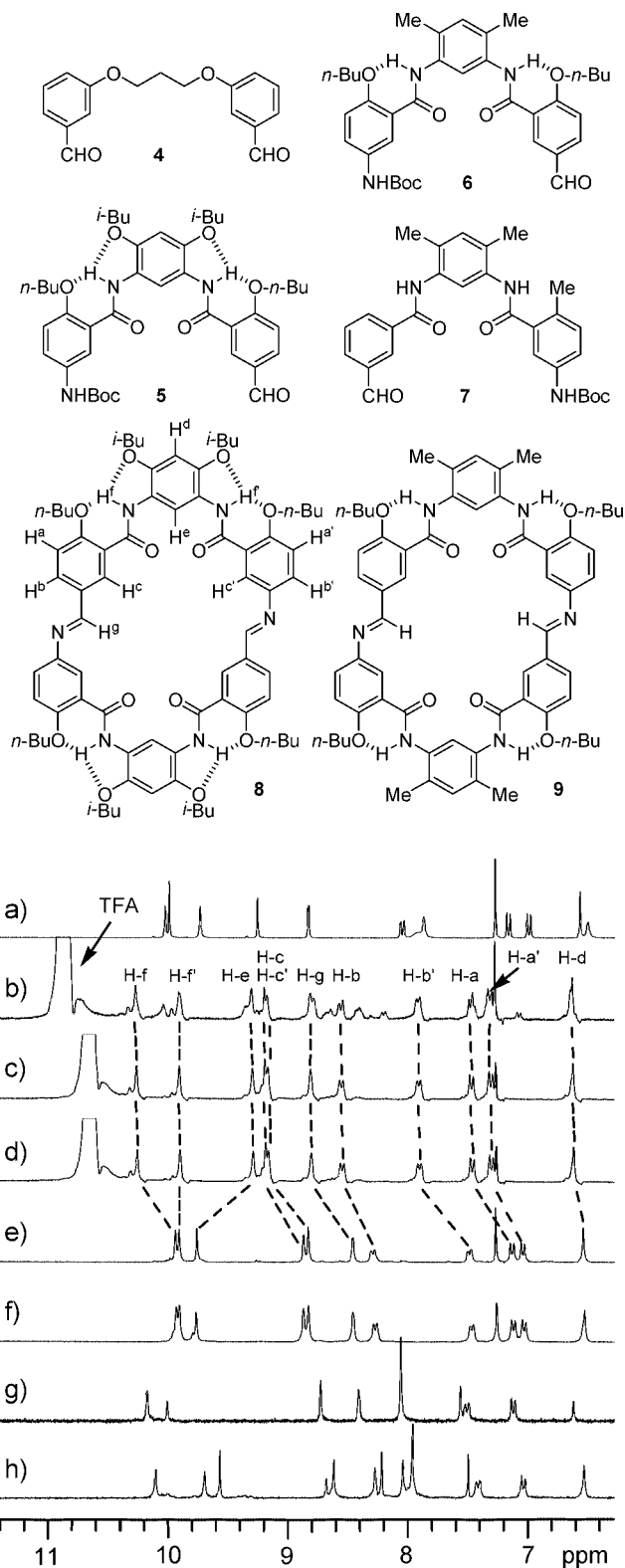


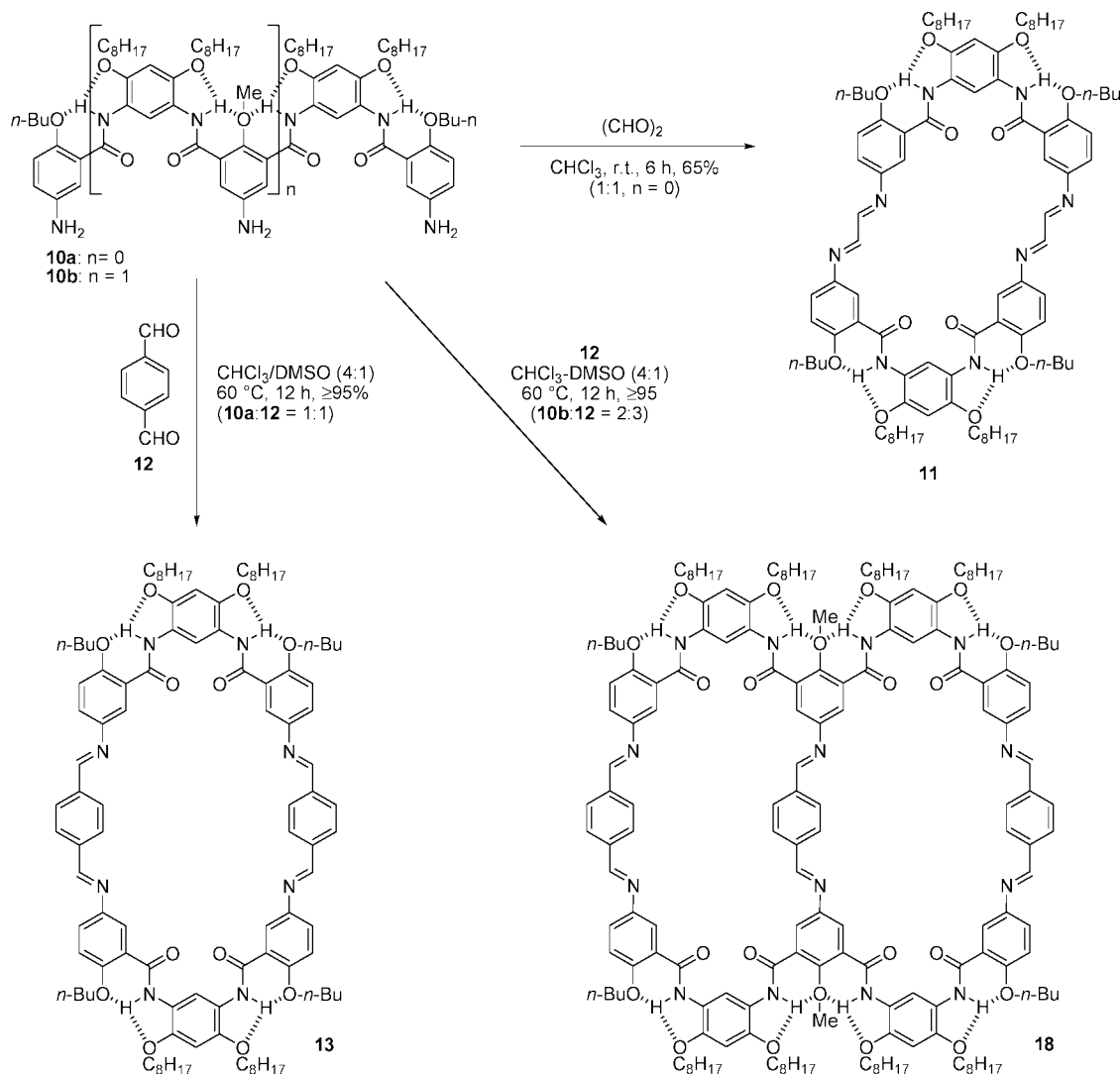
FIGURE 4. Partial ¹H NMR spectra of (a) **5**, (b) **5** + TFA (0.5 h), (c) **5** + TFA (1.5 h), (d) **8** + TFA (1.5 h), (e) **8** (crude product), (f) **8** (after recrystallization), (g) **13**, and (h) **18** ([**5**] = 5 mM, the concentration of other samples was 2.5 mM, [TFA] = 50 mM, see the structure of **8** for peak marking).

precursors not only highly facilitated the macrocyclization, but also promoted the conversion of their amino and aldehyde units into imines.

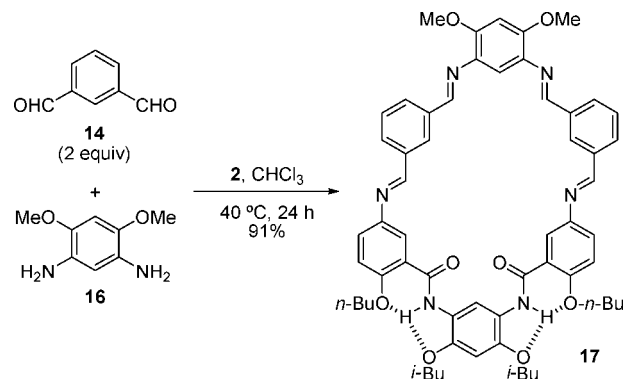
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SCHEME 2. Multicomponent Self-Assembly of Mono- and Bimacrocycles



Four-Component Condensation. Encouraged by the above results, the possibility of creating macrocycles from more components was then exploited. The first experiment concerned the [2+2] condensation reaction of preorganized diamines with dialdehydes. For this purpose, we replaced diamine **2** with **10a**, which carries two longer *n*-octyl groups, because the reactions of **2** in this series of experiments were found to afford insoluble residues that were difficult to characterize. The reaction of **10a** and oxalaldehyde (40% aqueous solution) was conducted in chloroform, which reached equilibrium after 6 h and afforded macrocycle **11** in 65% isolated yield (Scheme 2). The reaction of **10a** with **12** was carried out in the mixture of chloroform and DMSO (4:1). In this solvent system, no insoluble materials were formed, which guaranteed that the formation of products was thermodynamically controlled. The reaction reached equilibrium in 12 h to afford macrocycle **13** exclusively. Addition of TFA to the solution decreased the yield of the macrocycles, implying that the reaction equilibrium was shifted to the left. Increasing oxalaldehyde to 3 equiv did not obviously affect the yield of **11**, indicating that the macrocycle was much more stable than other possible products. The reactions of **10a** with isophthalaldehyde (**14**) or phthalaldehyde (**15**) were also investigated, which, however, did not generate corresponding [2+2] macrocyclic products in isolatable yields, once again indicating

SCHEME 3. Self-Assembly of Macrocycle 17 from [1+2+1] Condensation Reaction with Preorganized **2** as Template

that right geometry was indispensable for selective formation of the macrocyclic products.

Next, we investigated if this approach could be used for [1+2+1] macrocyclization. For this study, we chose compounds **2**, **14**, and **16** as precursors (Scheme 3). Stirring a solution of the three compounds (1:2:1) in chloroform led to the formation of macrocycle **17** in 91% isolated yield (Figure 6c, vide infra). In contrast, in the absence of **2**, the reaction of **14** and **16** (1:1)

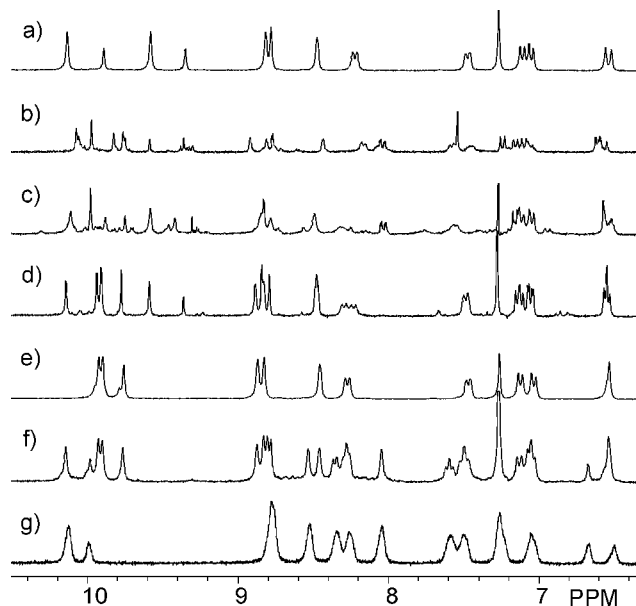


FIGURE 5. Partial ^1H NMR spectra of (a) **3**, (b) **1** + **2** + **5** (1:1:2) ($\text{CDCl}_3/\text{DMSO}-d_6$, 4:1), (c) **1** + **2** + **5** (1:1:2), (d) **3** + **8** (1:1), (e) **8**, (f) **8** + **17**, and (g) **17** in CDCl_3 . The concentration was 5 mM. The spectra of the crude products of **1**, **2**, and **5** were recorded after their TFA-catalyzed reactions in chloroform reached equilibrium and TFA was neutralized.

yielded no macrocyclic products but only simple linear molecules, as shown by the MS spectrum. Moreover, ^1H NMR showed that, after the reaction reached equilibrium, most of **14** and **16** were left unconsumed. A similar result was also observed for the reaction of **2** and **14** (1:1). However, when the two mixtures of the same equivalent were mixed together, **17** could be obtained in the same yield. The reaction of **2** and **16** with **12** or **15** was also attempted, from which no corresponding macrocyclic product was isolated. The fact that **17** was selectively formed from two distinct amine precursors should also be ascribed to the preorganization of precursor **2**.²⁵ Also owing to its high structural matching with **14** and **16**, **17** is expected to be much more stable than other cyclic or linear products. Therefore, it could be gradually enriched by consuming other less stable products.

Five-Component Condensation. The reaction of triamine **10b** and **12** (2:3) was first performed in chloroform. The reaction gave rise to precipitates immediately, which, however, did not dissolve even at the reflux temperature. MS spectrometry showed that the precipitates did contain bimacrocyclic **18** (Scheme 2). Therefore, discrete solvent systems were then screened, and finally we found that the binary system of chloroform and DMSO (4:1) yielded satisfactory results. In this medium, no precipitate was formed when the reaction was

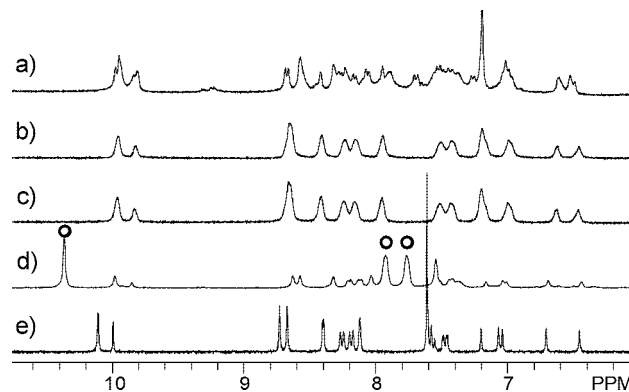


FIGURE 6. Partial ^1H NMR of (a) reaction residue of **2**, **14**, **15**, **16**, and **19** (1:2:1:2:2, after 24 h), (b) the product (**17**) after purification, and (c) **17** in CDCl_3 . Partial ^1H NMR of (d) reaction residue of **2**, **14**, **15**, and **16** (1:2:1:2, after 24 h) and (e) **17** in $\text{CDCl}_3/\text{DMSO}-d_6$ (4:1). The labeled signals belong to **15**.

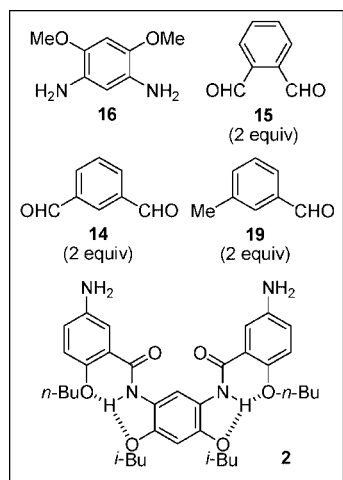
conducted at 60 °C. The reaction reached equilibrium after approximately 12 h, to afford **18** (Scheme 2). The ^1H NMR spectrum of **18** in $\text{CDCl}_3/\text{DMSO}-d_6$ (4:1) exhibited one set of signals of good resolution (Figure 4h), although configurational exchange of the three C=N bonds might give rise to different isomers. In principle, more complicated ladder oligomers or even polymers may be assembled from the longer multiamino precursors. However, the side chains have to be modified to provide enough solubility.

Self-Sorting and Selectivity Experiments. Self-Sorting is a stability-related behavior that features DCC in which multiple products may be formed from a multicomponent system.^{4,26} For the present structures, we chose three systems to study their selectivity behavior. The first system involved macrocycles **3** and **8** and their formation from coexisting precursors. ^1H NMR showed that mixing **3** and **8** (1:1) in CDCl_3 caused only a small amount of other molecules to form (Figure 5a,d,e). Mass spectrometry did not show the existence of larger products, including the possible trimer or tetramer, indicating good matching of the above precursors in macrocyclization. The mixture of **8** and **17** also exhibited similar self-fidelity (Figure 5e–g). Coexisting experiments showed that the precursors also possessed high self-sorting capacity in forming their respective macrocycles. For example, ^1H NMR indicated that, in the presence of TFA (10 equiv), the reaction of **1**, **2**, and **5** (1:1:2) in CDCl_3 reached equilibrium in 2 h. The ^1H NMR of the crude product, obtained after neutralization with no further purification, in $\text{CDCl}_3/\text{DMSO}-d_6$ (4:1) showed that **3** and **8** were formed as the two major products (Figure 5b). The spectrum of the same sample was also recorded in CDCl_3 , which showed that larger amounts of other products were formed (Figure 5c). This result is consistent with the above observation that higher macrocyclization selectivity could be achieved in the system of chloroform and DMSO than in pure chloroform.

The second system concerned the reaction selectivity of five molecules. Compounds **15** and **19** were chosen to compete with **14** for the reaction with **2** and **16** (Scheme 4). ^1H NMR showed that the reactions of **2**, **14**, **15**, **16**, and **19** (1:2:1:2:2) in CDCl_3 reached equilibrium in 24 h, giving rise to macrocycle **17** as the major product (Figure 6a). After recrystallizing the crude product from THF, **17** could be obtained in 56% yield (Figure 6b,c). In the absence of **19**, compounds **2**, **14**, and **16** could react to afford **17** nearly exclusively (Figure 6d,e). In this case, only isophthalaldehyde **14** was consumed, with phthalaldehyde

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SCHEME 4. Selective Formation of Macrocycle 17 from the Reactions of Five Precursors^a

^a In the absence of 19, 17 could be formed nearly exclusively from 2, 14, and 16.

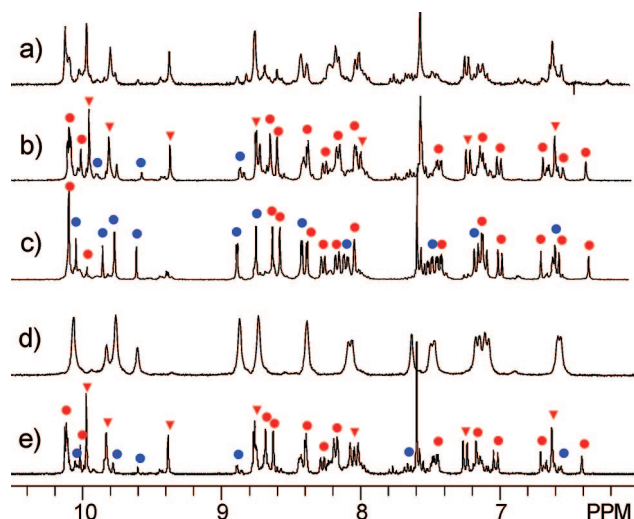


FIGURE 7. Partial ¹H NMR spectra of (a) the reaction mixture of 1, 14, and 16 (1:2:1), (b) 1, 14, 16, and 2 (1:2:1:1), (c) 1, 14, 16, and 2 (1:2:1:2), (d) 3, and (e) 3, 14, and 16 (1:2:1) in CDCl₃/DMSO-*d*₆ (4:1) (red triangle, 1; blue solid circle, 3; red solid circle, 17; [1] = 15 mM). All the spectra were recorded after the reactions reached equilibrium after 12 h.

15 being left. The result illustrates well the high capacity of 2 and 16 in selecting 14 to form a macrocyclic product.

The third system concerned the coexisting experiments of precursors 1, 2, 14, and 16. The ¹H NMR spectrum of the solution of 1, 14, and 16 (1:2:1) in CDCl₃ displayed complicated signals (Figure 7a), while the MS spectrum of the crude product did not exhibit molecular ion peaks of simple macrocyclic products but mainly those of linear imine species. These observations reflect poor structural matching of the three molecules. However, when 1 equiv of 2 was added (Figure 8), macrocycle 17 was generated in approximately 80% yield after the reaction reached equilibrium (Figure 7b). The yield was estimated by comparing the integrated intensity of its signal at 6.37 ppm and that of inner reference dibromomethane. In contrast, most of 1 was not consumed and thus only a small amount of 3 (ca. 5%) was formed. When another equivalent of 2 was added, it could selectively react with the remaining 1 to give 3 in approximately 85% yield, without affecting the

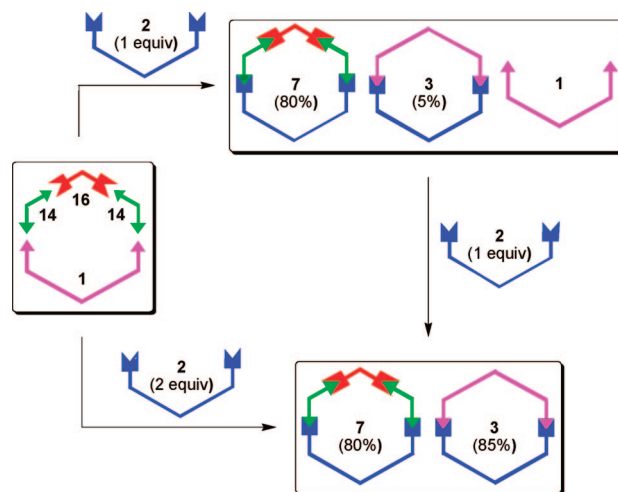


FIGURE 8. Hierarchical formation of macrocycles 3 and 17 from the solution of precursors 1, 2, 14, and 16 in CDCl₃/DMSO-*d*₆ (4:1), highlighting the high self-sorting capacity of the precursors in macrocyclization.

formation of 17 (Figure 7c). As expected, simultaneously mixing 1, 2, 14, and 16 (1:2:2:1) gave rise to the same result after the reactions reached equilibrium (Figure 8). These results indicated that in this system the formation of 3 and 17 from 2 occurred hierarchically. Only after the formation of the first favorable macrocycle 17 was met could the second one, that is 3, be generated. Whereas the ratio of the precursors was suitable, they could both be simultaneously generated in high yields. These results clearly indicate the high self-sorting capacity of the four precursors. The fact that 17 was formed prior to 3 from this four-component system does not imply that 17 was more stable than 3. More reasonably, it should reflect the feature of DCC that such thermodynamically controlled reactions prefer to afford products with least reactive sites left.^{7b} Additional evidence for this came from the observation that treatment of 3 with 14 (2 equiv) and 16 (1 equiv) caused most of the former to decompose, leading to the formation of 1 and 17 in approximately 80% yield (Figure 7d,e).

Intermacrocycle Imine–Hydrazone Exchange. Hydrazones are usually much more stable than imines because the mesomeric effect of hydrazones remarkably decreases their electrophilicity.²⁷ As an extension of this preorganization-driven macrocyclization, we also prepared compound 20 to assess its capacity of forming macrocycles. The related reactions were carried out at 60 °C in CHCl₃ and DMSO (4:1), in which both precursors and products were soluble. ¹H NMR showed that, in the absence of Lewis acid, 20 could react with 1 to afford macrocycle 21 quantitatively in 10 h (Scheme 5). Several reactions of forming hydrazone-based macrocycles have been reported to occur within days or weeks even under the catalysis of Lewis acid.^{8,28} It is reasonable to assume that the formation of the first hydrazone linkage is “normal”. Therefore, this result may be ascribed to the preorganization of the precursors that facilitated the formation of the second hydrazone bond intramolecularly, making it much faster. Macrocycle 21 could also be generated

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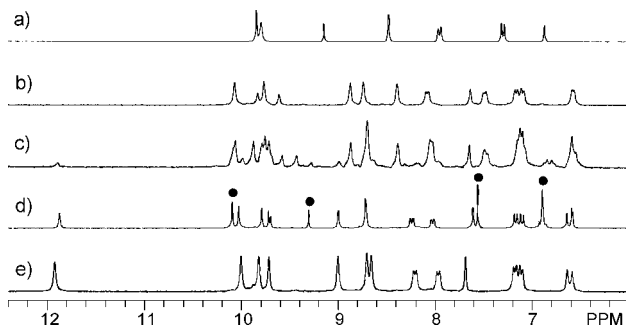
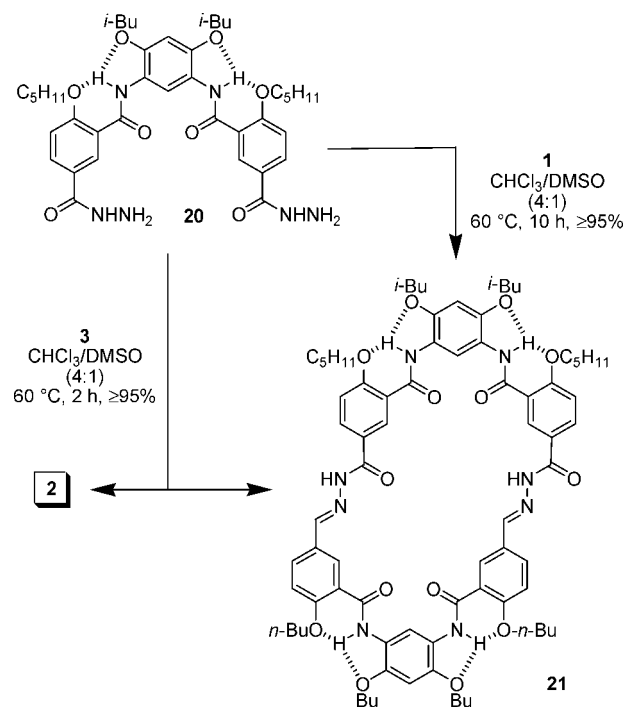


FIGURE 9. Partial ^1H NMR of (a) **20**, (b) **3**, (c) **3** + **20** (1:1, 5 min), (d) **3** + **20** (1:1, 2 h, the labeled signals belong to **2**), and (e) **21** in $\text{CDCl}_3/\text{DMSO}-d_6$ (4:1). The concentration was 5 mM.

SCHEME 5. Hydrazone-Based Macrocycle **21 from **1**+**1** Macrocyclization and Intercycle Imine–Hydrazone Exchange Reactions**



by treating macrocycle **3** with **20**. This intercycle imine–hydrazone exchange led to selective formation of **21** and **2** (Figure 9). Furthermore, this exchange reaction was finished in much shorter time (2 h). Because as electrophilic reagents aldehydes are usually more active than relevant imines,²⁷ this result appears to imply that the two exchange reactions occurred simultaneously and therefore could accelerate each other.

Conclusion

In this paper, we have demonstrated that intramolecular hydrogen bonding can be used to direct the thermodynamically controlled formation of imine- and hydrazone-based macrocyclic structures by modulating the conformation or shape of one or more molecular components. This modulation is workable in less polar and polar solvents and even in the presence of excess strong protonic acid like TFA. The construction of the bimacrocyclic through the formation of six imine bonds from six components illustrates well the efficiency of this new approach. Since the intramolecular hydrogen bonding patterns have been evidenced to occur in polar

solvents,^{16a,e} the reactions could be extended into polar solvents. The high conformational predictability of this family of hydrogen bonded aromatic amide oligomers also makes them potentially useful as templating backbones for the synthesis of one-dimensional nanoarchitectures.

A notable feature of this hydrogen bonding-directed DCC is that the components can be readily expanded and functionalized, whereas the size of the macrocyclic units can also be tuned by regulating the distance of the reactive sites. In principle, any reactive sites that undergo reversible covalent reactions can be introduced to the amide backbones, while DCC of similar polymeric precursors may lead to the construction of porous tapes of long-range order. Therefore, the work also opens up a new possibility for quick construction of more complicated porous systems.

Experimental Section

Compound 3. A solution of **1** (52 mg, 0.08 mmol) and **2** (51 mg, 0.08 mmol) in chloroform (8 mL) was stirred at room temperature for 15 h and then concentrated and dried under reduced pressure. The resulting residue was recrystallized from acetonitrile and chloroform to give compound **3** as a yellow solid (75 mg, 75%). ^1H NMR (CDCl_3) δ 10.13 (s, 2 H), 9.89 (s, 1 H), 9.58 (s, 2 H), 9.35 (s, 1 H), 8.81 (s, 2 H), 8.78 (s, 2 H), 8.47 (d, $J = 1.5$ Hz, 2 H), 8.22 (d, $J = 8.4$ Hz, 2 H), 7.47 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 2 H), 7.10 (d, $J = 8.4$ Hz, 2 H), 7.05 (d, $J = 8.5$ Hz, 2 H), 6.53 (d, $J = 11.8$ Hz, 2 H), 4.44–4.09 (m, 8 H), 3.84 (d, 8 H), 2.17–2.14 (m, 4 H), 1.95–1.91 (m, 8 H), 1.64–1.34 (m, 8 H), 1.14–1.01 (m, 18 H), 0.99–0.96 (m, 12 H); ^{13}C NMR (CDCl_3) δ 162.8, 162.4, 159.5, 158.5, 155.1, 146.2, 145.3, 144.8, 137.7, 129.9, 129.8, 128.2, 124.1, 123.3, 123.0, 122.1, 121.0, 119.0, 115.9, 113.7, 113.1, 98.6, 98.1, 75.9, 69.9, 69.5, 31.0, 28.3, 19.4, 19.3, 19.1; MS (MALDI-TOF) m/z 1259 [$\text{M} + \text{H}$]⁺, 1281 [$\text{M} + \text{Na}$]⁺; HRMS (MALDI-TOF) calcd for $\text{C}_{74}\text{H}_{95}\text{N}_6\text{O}_{12}$ 1259.7035, found 1259.7003.

Compound 8. A solution of compound **5** (0.30 g, 0.40 mmol) and TFA (0.46 g, 4.00 mmol) in chloroform (10 mL) was stirred at room temperature for 1.5 h. To the solution was added saturated sodium bicarbonate solution (10 mL). The mixture was stirred for 10 min and the organic phase was separated with a separating funnel. The aqueous solution was extracted with chloroform (3 \times 5 mL). The organic phases were combined and washed with water (10 mL) and brine (10 mL) and dried over sodium sulfate. The solution was concentrated and the resulting residue washed with ether and dried under vacuum to give compound **8** as a yellow solid (0.26 g, 100%). ^1H NMR (CDCl_3) δ 9.92 (s, 2 H), 9.89 (s, 2 H), 9.76 (s, 2 H), 8.87 (s, 2 H), 8.83 (s, 2 H), 8.46 (s, 2 H), 8.27 (d, $J = 10.1$ Hz, 2 H), 7.47 (d, $J = 8.8$ Hz, 2 H), 7.12 (d, $J = 8.8$ Hz, 2 H), 7.03 (d, $J = 10.1$ Hz, 2 H), 6.53 (s, 2 H), 4.35–4.27 (m, 8 H), 3.88–3.83 (m, 8 H), 2.19–2.13 (m, 4 H), 1.96–1.87 (m, 8 H), 1.49–1.47 (m, 8 H), 1.07–0.98 (m, 36 H); MS (MALDI-TOF) m/z 1259 [$\text{M} + \text{H}$]⁺, 1282 [$\text{M} + \text{Na}$]⁺; HRMS (MALDI-TOF) calcd for $\text{C}_{74}\text{H}_{94}\text{N}_6\text{O}_{12}\text{Na}$ [$\text{M} + \text{Na}$]⁺ 1281.6822, found 1281.6806. Anal. Calcd for $\text{C}_{74}\text{H}_{94}\text{N}_6\text{O}_{12} \cdot \text{H}_2\text{O}$: C, 69.57; H, 7.57; N, 6.08. Found: C, 69.41; H, 7.28; N, 6.50.

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Supporting Information Available: General methods, detailed synthesis and characterizations, ^1H NMR spectra, MS spectra of two reaction mixtures, and CIF files of **1**–**3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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