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Triptycene-Based Expanded Oxacalixarenes: Synthesis, Structure, and Tubular Assemblies in the Solid State

Chun Zhang[†,‡] and Chuan-Feng Chen*[,†]

Beijing National Laboratory for Molecular Sciences, Laboratory of Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School, Chinese Academy of Sciences, Beijing 100049, China

cchen@iccas.ac.cn

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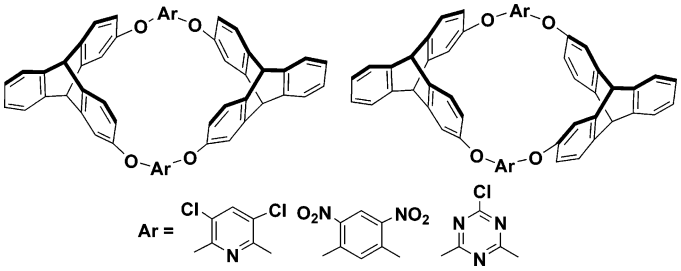

Owing to the unique 3D rigid structure of triptycene, two novel expanded oxacalixarenes **5a** and **5b** as a pair of diastereomers were efficiently synthesized in a single step by the S_NAr reaction of 2,7-dihydroxytriptycene with 2,3,5,6-tetrachloropyridine in the presence of cesium carbonate. Similarly, two pairs of other triptycene-based expanded oxaxalixaenes **7a**,**7b** and **9a**,**9b** could also be obtained by the S_NAr reactions of 2,7-dihydroxytriptycene with 1,5-difluoro-2,4-dinitrobenzene and cyanuric chloride, respectively. The structures of the expanded oxacalixarenes were studied by NMR, MS spectra, and X-ray crystal structure analyses. It was found that the expanded oxacalixarene **9b** showed a dynamic interconversion between boat and chair conformations. Moreover, we also found that the expanded oxacalixarenes **5a**, **5b**, and **9a** could all assemble into organic tubular structures and further porous architectures in the solid state, in which chlorine bonding, such as C−Cl···Cl, C−Cl···O, and C−Cl···π interactions, played an important role.

Introduction

Heterocalixarenes,[1,2] in which the carbon linkages between the aromatic units are replaced by heteroatoms, are of current interest in calixarene chemistry for their ready availability, tunable cavities, and potential applications in supramolecular chemistry. Oxacalixarenes[3] are a class of important heterocalixarenes, and they have attracted increased interest in recent years. Consequently, different methods for the synthesis of oxacalixarenes have been developed.[4,5] In particular, Katz et al.[5a−c] reported a single-step synthesis of a series of functionalized

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Graduate School, Chinese Academy of Sciences.

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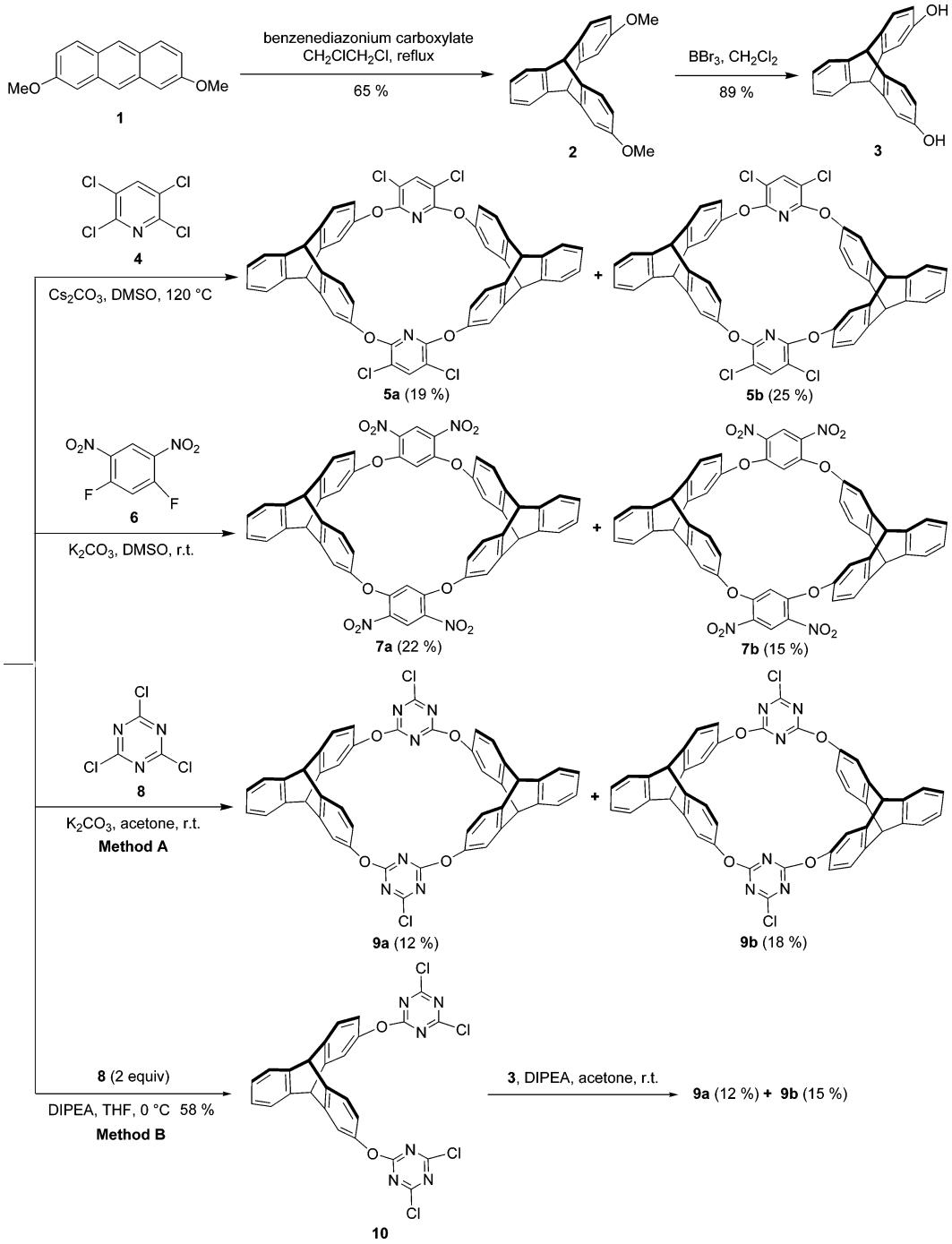
SCHEME 1. Synthesis of the Expanded Oxacalixarenes



oxacalix[4]arenes in high yields through nucleophilic aromatic substitution (S_NAr) reactions, which is an important breakthrough in oxacalixarene chemistry. However, little is so far known about the macrocycles with large cavities,[4c,5d,e] such as oxacalix[6]arenes and oxacalix[8]arenes. Moreover, the small cavities or flexible conformations of the known oxacalixarenes may also limit their applications in supramolecular chemistry. These problems will provide chemists with many opportunities and challenges in this research field.

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TABLE 1. X-ray Crystallographic Data of the Oxacalixarenes

compound	**5a**·2CH_2Cl_2·$(C_2H_5)_2O$	**5b**·2CH_2Cl_2	**9a**
formula	$C_{56}H_{40}Cl_8N_2O_5$	$C_{52}H_{30}Cl_8N_2O_4$	$C_{46}H_{24}Cl_2N_6O_4$
M_r	1104.5	1030.38	795.61
crystal system	monoclinic	triclinic	monoclinic
space group	*C*2/c	*P*-1	*C*12/c1
a (Å)	25.454(3)	8.7116(17)	41.277(15)
b (Å)	11.0665(14)	9.7063(19)	19.829(6)
c (Å)	18.796(2)	13.761(3)	29.101(10)
α (deg)	90	95.19(3)	90
β (deg)	103.541(2)	93.16(3)	119.396(4)
γ (deg)	90	96.43(3)	90
V (Å^3)	5147.5(11)	1149.0(4)	20752(12)
Z	4	1	12
d	1.425	1.489	0.764
T (K)	294(2)	293(2)	293(2)
GOF on F^2	1.010	1.033	0.971
R_1 [$I > 2\sigma(I)$]	0.0609	0.0729	0.0835
wR_2 (all data)	0.2018	0.2136	0.2605

Organic tubular assemblies[6,7] have been the subject of increased attention due to their wide potential applications in chemical, biological, and material sciences. As a result, various organic tubular systems with different interior properties have been developed. It is noteworthy that studies on the calixarene-based tubular assemblies[8] are scattered, although they may be useful for the recognition and transport of aromatic molecules.

Recently, we became interested in the synthesis and properties of some novel receptors based on the triptycene[9] with unique 3D rigid structure, which resulted in the development of some new supramolecular systems.[10] We envisioned that if 2,7-dihydroxytriptycene instead of *m*-diphenol was used as the nucleophilic coupling partner for synthesis of oxacalixarenes by the S_NAr reactions, large macrocyclic compounds with specific structures and properties could be formed. Herein, we report the efficient synthesis, structure, and tubular assemblies in the solid state of a series of novel triptycene-based expanded oxacalixarenes. Owing to the 3D rigid structure of triptycene, a pair of diastereomers in each case could be obtained by the S_N2 reaction of 2,7-dihydroxytriptycene with an electrophilic component, and a dynamic interconversion between boat and chair conformations could also be observed. Moreover, it was found that the expanded oxacalixarenes containing chlorine could assemble into organic tubular structures and further porous architectures in the solid state, in which chlorine bonding, such as C−Cl···Cl,[11] C−Cl···O,[12] and C−Cl···π[13] interactions, played an important role.

Results and Discussion

Syntheses of the Expanded Oxacalixarenes. Synthesis of the expanded oxacalixarenes is depicted in Scheme 1. 2,7-Dimethoxyanthracene **1** was prepared according to the literature method.[14] Diels−Alder reaction of **1** and benzenediazonium carboxylate in 1,2-dichloroethane resulted in the triptycene derivative **2** in 65% yield, which was then demethylated with BBr_3 to give the 2,7-dihydroxytriptycene **3** in 89% yield. Compound **3** is an important precursor for synthesis of the expanded oxacalixarenes.

We first tested the coupling reaction of 2,7-dihydroxytriptycene **3** and 2,3,5,6-tetrachloropyridine **4** in DMSO in the presence of Cs_2CO_3 and found that the expanded oxacalixarenes **5a** and **5b** could be obtained in 19% and 25% yield, respectively. Similarly, the expanded oxacalixarenes **7a** and **7b** could also be synthesized in 22% and 15% yield, respectively, by the S_N2 reaction of the compound **3** and 1,5-difluoro-2,4-dinitrobenzene **6** in the presence of K_2CO_3.

Under the coupling conditions as above, expanded oxacalixarenes **9a** and **9b** might be unstable, so they could not be obtained. But under various conditions examined, we found that **9a** and **9b** could be synthesized in a single step by the reaction of **3** with cyanuric chloride **8** in acetone in the presence of K_2CO_3 (method A). Compounds **9a** and **9b** could also be synthesized by a two-step method (method B). Consequently, the reaction of **3** and 2 equiv of cyanuric chloride **8** in tetrahydrofuran in the presence of diisopropylethylamine (DIPEA) afforded the linear product **10** in 58% yield. The macrocyclic coupling reaction between **3** and **10** in acetone with DIPEA as base then took placed at room temperature, which resulted in the expanded oxacalixarenes **9a** and **9b** in 12% and 15% yield, respectively.

Structures of the Expanded Oxacalixarenes. There exist two possible linking modes of 2,7-dihydroxytriptycene **3** for

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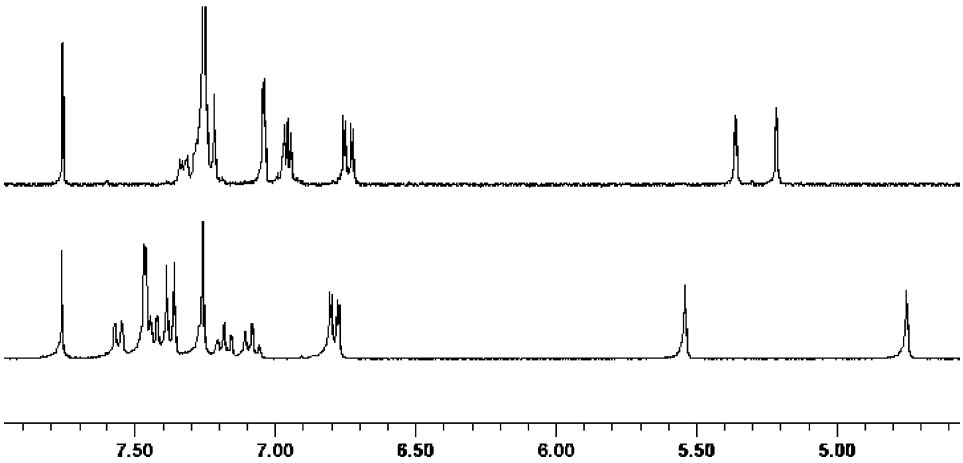

FIGURE 1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **5a** (up) and **5b** (down).

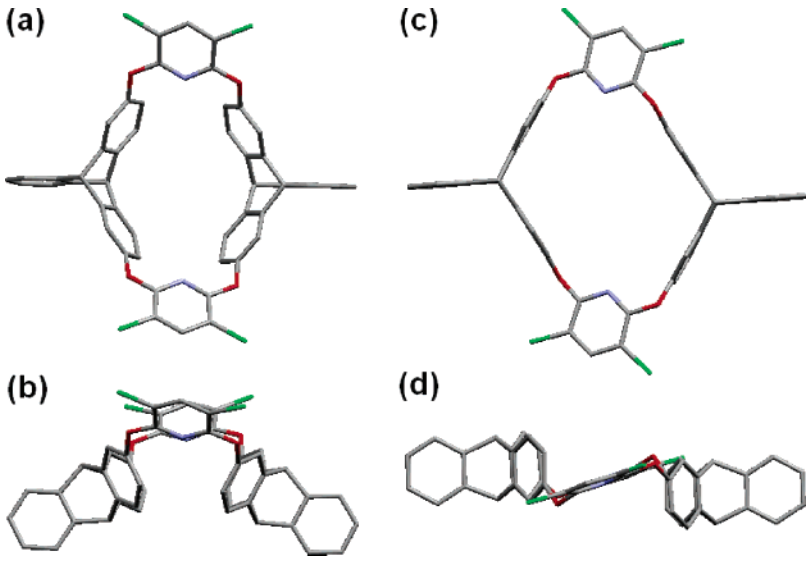

FIGURE 2. Crystal structures. (a) Top view and (b) side view of **5a**; (c) top view and (d) side view of **5b**. Solvent molecules and hydrogen atoms are omitted for clarity.

the S_NAr coupling reaction due to its 3D rigid structure. Consequently, the expanded oxacalixarenes **5a** and **5b** were formed by reaction of **3** and 2,3,5,6-tetrachloropyridine **4**, and they could be easily separated by column chromatography over silica gel with 1:2 CH_2Cl_2/petroleum ether as the eluent, in which compound **5a** ($R_f = 0.36$) showed a bigger polarity than that of compound **5b** ($R_f = 0.43$). It was found that the MALDI-TOF mass spectra of compounds **5a** and **5b** all revealed the peak at *m*/*z* 860.7 for M^+, which suggested that they are a pair of diastereomers. The ^{1}H NMR spectrum of the isomer **5a** showed only two singlets for the bridgehead (or methenyl) protons and one singlet for the protons of pyridine moieties; meanwhile, its ^{13}C NMR spectrum showed only two signals for the bridgehead carbons. These results are all consistent with its C_2 symmetry. Similarly, the isomer **5b** also has a C_2 symmetric structure, which was established by its ^{1}H NMR and ^{13}C NMR spectra. Due to different linking modes of the triptycene moieties, the isomers **5a** and **5b** showed different triptycene proton signals in their ^{1}H NMR spectra (Figure 1). For the cis isomer **5a**, close chemical shifts of the aromatic protons and small different shifts for the methenyl protons with $\Delta\delta$ of 0.15 ppm were observed. For the trans isomer **5b**, it was found that not only the aromatic proton signals of the triptycene moiety split very well, but also the two methenyl protons showed significant different chemical shifts with $\Delta\delta$ of 0.79 ppm. These observations may be attributed to the very different shielding or deshielding effect of the pyridine group to the triptycene protons of **5b**.

The X-ray crystal structure analyses of **5a** and **5b** (Table 1, Figure 2) further revealed that they are a pair of diastereomers, in which **5a** is a cis isomer (boat form) and **5b** is a trans isomer (chair form). Similar to other oxacalixarenes, **5a** is in a 1,3-alternate conformation. The dihedral angle between the two pyridine rings is 69.79°, while the dihedral angles between two pairs of face-to-face benzene rings are 43.13° and 50.74°, respectively. The macrocycle **5a** has a boatlike conformation with a cavity cross-section from 8.66 × 13.20 Å (upper rim) to 6.28 × 8.65 Å (low rim). Moreover, it was also found that the two nitrogen atoms in **5a** point inward while four chlorines point outward. This structural feature will be a benefit to its assembly in the solid state. For **5b**, the two pyridine rings are parallel each other and inclined by 8.57° to the plane formed by four

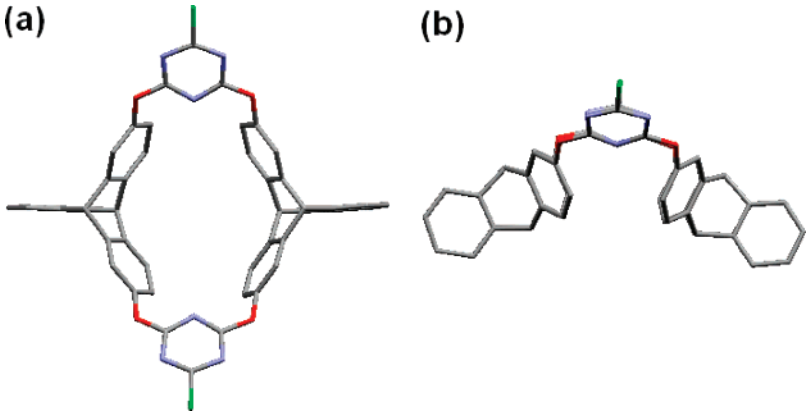

FIGURE 3. (a) Top view and (b) side view of the crystal structure of **9a**.

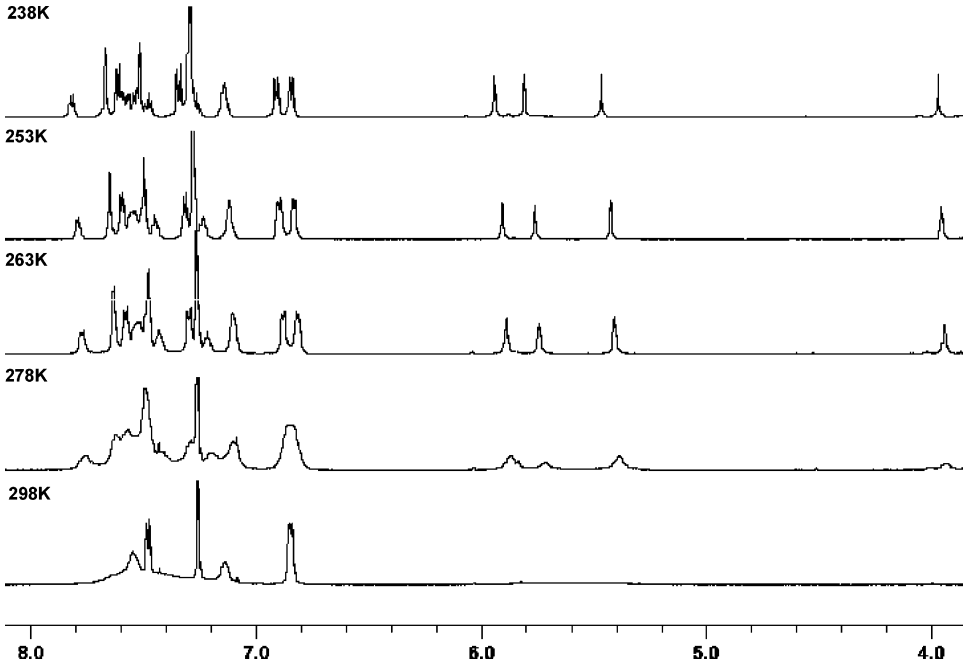

FIGURE 4. ^{1}H NMR spectra of **9b** (600 MHz, $CDCl_3$) at different temperatures.

bridging oxygen atoms. The centroid distances between two pairs of face-to-face paralleled benzene rings are 7.36 and 8.88 Å, respectively. Moreover, the two nitrogen atoms point inward with a distance of 8.55 Å, while four chlorines point outward, which is similar to those of **5a**.

The expanded oxacalixarenes **7a** and **7b** have low solubility in most common polar and nonpolar solvents, but they showed good solubility in dichloromethane. They were all characterized by ^{1}H NMR, ^{13}C NMR, and MS spectra. The MALDI-TOF MS spectra of **7a** and **7b** showed that they are a pair of diastereomers with the same molecular ion peak at *m*/*z* 900.9 for M^+. In comparison with the ^{1}H NMR spectra of the isomers **7a** and **7b**, and the isomers **5a** and **5b**, it could be found that **7a** has a split mode similar to that of **5a**, while **7b** has a split mode similar to that of **5b**. Moreover, the polarity order for the isomers in CH_2Cl_2 and petroleum ether (5:1) was found to be **7a** > **7b**, which is also similar to the case of the isomers **5a** and **5b**. These observations suggested that **7a** is a cis isomer and **7b** is a trans isomer.

The oxacalixarenes **9a** and **9b** are also a pair of diastereomers, and they all have good solubility in common solvents. Compound **9a** was determined to be a cis isomer, and its ^{1}H NMR spectrum showed split modes of triptycene protons similar to those of **5a**. Moreover, we obtained a single crystal of **9a** suitable for X-ray diffraction by slow evaporation of the $CHCl_3$ solution (Table 1), which provided direct evident for the structure of **9a**. As shown in Figure 3, the cis isomer **9a** has a similar 1,3-alternate conformation to **5a**, and the chlorines all point outward. Moreover, it was found that there exist two molecules of **9a** with different orientations in its crystal cell. In one molecule, the dihedral angle between the two trizine rings is 77.0°, and the dihedral angles between two pairs of face-to-face benzene rings are 40.79° and 45.87°, respectively. Similar to **5a**, the boatlike conformation of the molecule **9a** has a cavity cross-section from 8.67 × 12.90 Å (upper rim) to 6.46 × 8.55 Å (low rim). In another molecule, the dihedral angle between the two trizine rings is 67.2°, while the dihedral angles between two pairs of face-to-face benzene rings are 28.66° and 40.62°,

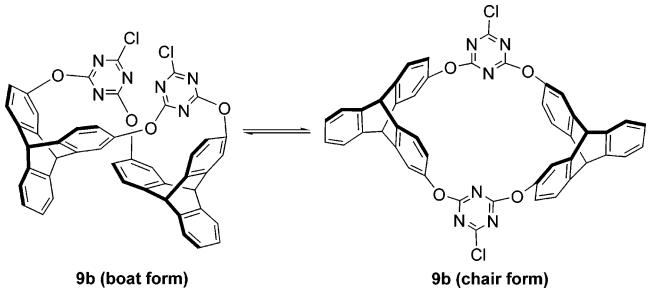

FIGURE 5. Proposed dynamic interconversion between different conformations of **9b**.

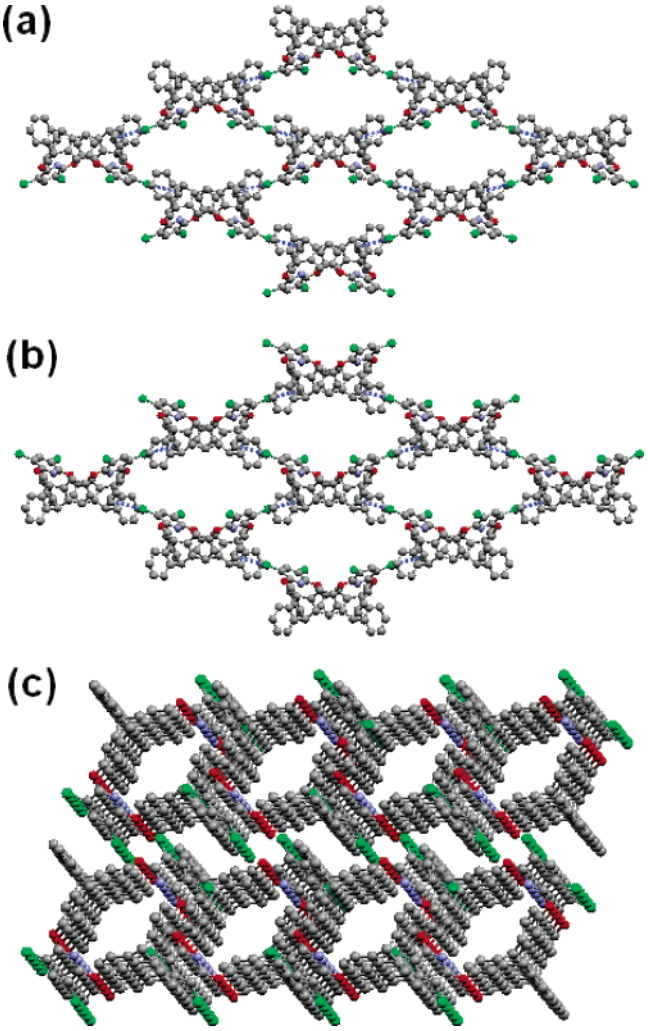

FIGURE 6. Packing of **5a**. Two adjacent layers: (a) layer A and (b) layer B viewed along the *c*-axis. Dashed lines show the C−Cl···π interactions. (c) One channel viewed along the *b*-axis. Solvent molecules and hydrogen atoms are omitted for clarity.

respectively. The boatlike conformation of the molecule has a cavity cross-section from 8.92 × 12.59 Å (upper rim) to 7.12 × 8.45 Å (low rim).

In comparison with the NMR spectra of **5b** and **7b**, oxacalixarene **9b** in $CDCl_3$ showed very broadened proton signals at room temperature, which might be due to a dynamic behavior of interconversion between the boat and chair conformations. Consequently, the variable-temperature NMR experiments of

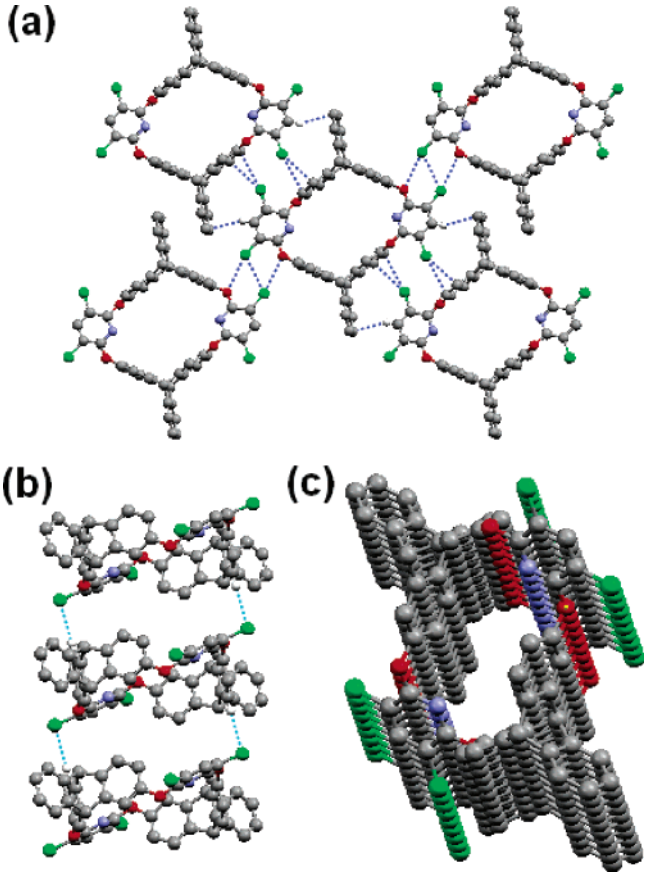

FIGURE 7. Packing of **5b**. (a) View of multiple noncovalent interactions (dashed lines) between one molecule and its adjacent molecules. (b) Side view of a tubular organization. (c) View of a tubular assembly with the aromatic rings as the wall along the *a*-axis. Solvent molecules and hydrogen atoms not involved in the interactions are omitted for clarity.

9b were carried out. As shown in Figure 4, the broadened signals for the triptycene protons are gradually distinct with the decrease of the temperature and split very well into two sets of proton signals at 238 K. Moreover, a significant upfield shift (δ = 3.9 ppm) for a methenyl proton was observed, which might be due to the strong shielding effect of aromatic rings of the other triptycene moiety. These observations suggested that the molecule **9b** might adopt a stable boat conformation at lower temperature, in which the two triptycene moieties are different. Furthermore, it was also found that the broadened triptycene signals split distinctly into only one set of signals at 328 K, which might be attributed to the rapid interconversion of different conformations of **9b** over the NMR time scale. In combination with its crystal structure,[15] a dynamic interconversion between boat and chair conformations of **9b** was proposed (Figure 5).

Tubular Assemblies of Expanded Oxacalixarenes in the Solid State. We first studied the self-assembly of expanded oxacalixarene **5a** in the solid state and found that it could take an indirect ring-stacking mode to form a tubular assembly.[7h] Bridged by the adjacent molecules, tubular assembly of **5a** in

(15) Owing to the poor quality of the crystal of **9b**, the diffraction intensity was weak, which resulted in an uncompleted structural solution. However, it could be found from the preliminary result that the oxacalixarene **9b** is a trans isomer with a boat conformation.

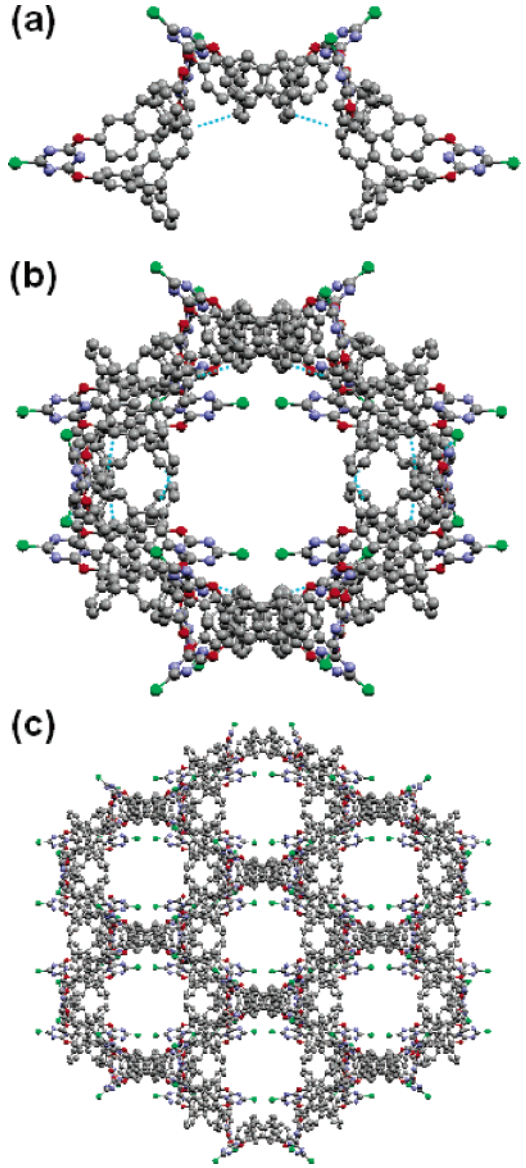

FIGURE 8. Packing of **9a**. (a) View of an arc structure. (b) A view of the tube along the *c*-axis. (c) One channel viewed along the *c*-axis. Hydrogen atoms are omitted for clarity.

which the wall also consists of aromatic rings is thus formed by the intermolecular complementary C−Cl···π ($d_{C-Cl\cdots\pi}$ = 3.24 Å) interactions between one macrocyclic molecule and its adjacent bridged ones.[16] During the formation of the tube, there exist two different layers (A and B) in which the tubular assemblies are in opposite directions (Figure 6a,b). In each layer, it was found that a rhombic cavity with the cross-section of ca. 13.88 × 13.88 Å is formed by four bridging macrocyclic molecules. Furthermore, by virtue of $\pi\cdots\pi$ ($d_{\pi\cdots\pi}$ = 3.34 Å) stacking and a pair of complementary C−H···π ($d_{C-H\cdots\pi}$ = 2.79 Å) interactions, the layers stack alternately in an AB sequence to result in bidirectional channels.[7g] One channel viewed along the *b*-axis is resulted from the boatlike conformation of the macrocycle (Figure 6c), and the other one viewed along the *c*-axis is attributed to the stacking of the macrocyclic portion of the assembly.[16]

(16) See the Supporting Information.

Interestingly, it was found that there are 18 noncovalent interactions between the macrocyclic molecule **5b** and its adjacent six molecules, in which 14 interactions are relevant to all of the chlorines in **5b** (Figure 7a). By a pair of complementary C−H···Cl interactions[11b] ($d_{H\cdots Cl}$ = 2.78 Å, $\theta_{C-H\cdots Cl}$ = 164.0°) between the adjacent molecules, the macrocycles of **5b** can also stack into a tubular structure (Figure 7b).[16] It is noteworthy that the wall of this tubular channel consists of benzene rings linked with oxygen atoms, and the nitrogen atoms of the pyridine rings all point inward toward the tube (Figure 7c). These characteristics may impart the tube unique structural features, which are different from those of previously reported organic tubular assemblies.[7] It was also found that the tubes can further self-assemble into high order superstructure and the multiple chlorine bondings play an important role in the assembly processes. Consequently, the tubes associate with each other to form a 2D layer by virtue of a pair of complementary C−Cl···π ($d_{C-Cl\cdots\pi}$ = 3.34 Å) and a pair of complementary C−H···π ($d_{C-H\cdots\pi}$ = 2.80 Å) interactions between one macrocycle and its adjacent molecules. The layers further interact on each other by combination of a pair of complementary C−Cl···O ($d_{Cl\cdots O}$ = 3.26 Å, $\theta_{C-Cl\cdots O}$ = 159.4°) and C−Cl···Cl ($d_{Cl\cdots Cl}$ = 3.38 Å, $\theta_{C-Cl\cdots Cl}$ = 112.8°) interactions between the two adjacent macrocyclic molecules, which results in two sets of perpendicular channels.[16] In the channel viewed along the *a*-axis, CH_2Cl_2 molecules are located, which shows the hydrophobic character of the inner face of the tubular assembly.[7c,16]

The oxacalixarene **9a** can also assemble into a tubular superstructure in the solid state, but it takes a different assembled mode from those of **5a** and **5b**. As shown in Figure 8a, the neighboring three molecules of **9a** are connected by each other to form an arclike structure through C−H···π ($d_{C-H\cdots\pi}$ = 2.86 Å) interaction. The adjacent arc structures are then connected with two molecules of **9a** in different orientations, which results in a hollow structure by four pairs of C−H···π ($d_{C-H\cdots\pi}$ = 2.87 Å and 2.89 Å) interactions[16] and a further tubular assembly by a couple of C−H···Cl ($d_{H\cdots Cl}$ = 2.86 Å, $\theta_{C-H\cdots Cl}$ = 161.6°) interactions (Figure 8b). During the formation of the tube, there exist two different layers (A and B), and in each layer a rhombic cavity with the cross section of ca. 22.90 × 22.90 Å is formed by six bridging macrocyclic molecules.[16] Moreover, it was also found that by virtue of C−Cl···Cl ($d_{Cl\cdots Cl}$ = 3.27 Å, $\theta_{C-Cl\cdots Cl}$ = 145.7°) and $\pi\cdots\pi$ ($d_{\pi\cdots\pi}$ = 3.67 Å) interactions, the layers can stack alternately in an AB sequence to result in a large channel viewed along the *c*-axis (Figure 8c).

Conclusions

We have synthesized three pairs of novel triptycene-based expanded oxacalixarenes by the S_N2 reactions of 2,7-dihydroxytriptycene with 2,3,5,6-tetrachloropyridine, 1,5-difluoro-2,4-dinitrobenzene, and cyanuric chloride, respectively. Owing to the 3D rigid structure of the triptycene, both cis and trans isomers in each S_N2 reaction were obtained, and a dynamic interconversion between boat and chair conformations of the oxacalixarene **9b** was also observed. Moreover, we found that the expanded oxacalixarenes **5a**, **5b**, and **9a** could assemble into organic tubular structures and further porous architectures in the solid state, in which multiple chlorine bonds including C−Cl···Cl, C−Cl···O, and C−Cl···π interactions played an important role. The present results will provide us the op-

portunity to develop new supramolecular systems with specific structures and properties, which are underway.

Experimental Section

Compound 2. A mixture of 2,7-dimethoxyanthracene (1.30 g, 5.5 mmol), benzenediazonium carboxylate (4.78 g, 27.5 mmol), and 1,2-epoxypropane (10 mL) in dichloroethane (100 mL) was refluxed overnight and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 1:6 CH_2Cl_2/petroleum ether) to afford 1.12 g (65%) of **2** as a white solid. Mp: 153−154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 (s, 6H), 5.28 (s, 1H), 5.29 (s, 1H), 6.48 (dd, J = 8.1, 2.4 Hz, 2H), 6.95−7.00 (m, 4H), 7.24 (d, J = 8.1 Hz, 2H), 7.31−7.37 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.3, 54.5, 55.4, 109.2, 110.4, 123.1, 123.5, 123.8, 124.9, 125.3, 138.1, 144.9, 146.1, 146.6, 157.1. EI MS: m/z 314 (M^+). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.88; H, 5.89.

Compound 3. To a solution of **2** (0.45 g, 1.5 mmol) in dry dichloromethane (50 mL) in an ice bath was added boron bromide in dichloromethane (6.0 mL, 1 M). After the reaction mixture was stirred at rt for 6 h and then refluxed for 2 h, it was cooled to rt and hydrolyzed with hydrochloric acid (0.1 M, 10 mL). The aqueous layer was extracted twice with dichloromethane (2 × 10 mL) and twice with diethyl ether (2 × 10 mL). The organic layers were combined, washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 1:3 acetone/petroleum ether) to afford 0.38 g (89%) of **3** as a white solid. Mp: 217−218 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 5.36 (s, 1H), 5.37 (s, 1H), 6.41 (dd, J = 7.9, 2.4 Hz, 2H), 6.96 (d, J = 2.4 Hz, 2H), 6.93−6.96 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.33−7.39 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 53.0, 54.9, 111.3, 112.6, 123.7, 124.3, 124.6, 125.4, 125.8, 138.2, 146.6, 147.9, 148.0, 155.5. HRMS calcd for $C_{20}H_{14}O_2$: $[M]^+$ 286.0994, found 286.0992.

Synthesis of 5a and 5b. Under a dry argon atmosphere, a mixture of **3** (0.34 g, 1.2 mmol), 2,3,5,6-tetrachloropyridine (0.61 g, 1.2 mmol), and anhydrous Cs_2CO_3 (0.97 g, 3.0 mmol) in anhydrous DMSO (25 mL) was stirred vigorously at 120 °C for 12 h and then cooled to rt. The reaction mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (40 mL) and separated, and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (eluent: 1:2 CH_2Cl_2/petroleum ether) to give 0.10 g (19%) of **5a** (R_f = 0.36) and 0.13 g (25%) of **5b** (R_f = 0.43) as white solids. **5a**. Mp > 300 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.19 (s, 2H), 5.34 (s, 2H), 6.70 (dd, J = 8.1, 2.3 Hz, 4H), 6.88−6.90 (m, 4H), 6.95 (d, J = 2.3 Hz, 4H), 7.20−7.25 (m, 6H), 7.27−7.31 (m, 2H), 7.72 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 53.0, 54.0, 112.0, 116.5, 117.1, 123.5, 123.7, 124.0, 125.6, 125.7, 141.89, 141.91, 145.2, 146.0, 146.8, 150.2, 154.4. MALDI TOF-MS: m/z 860.7 (M^+). Anal. Calcd for $C_{50}H_{26}Cl_4N_2O_4 \cdot 0.5CH_2Cl_2$: C, 67.17; H, 3.01; N, 3.10. Found: C, 66.88; H, 3.21; N, 2.98. **5b**. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75 (s, 2H), 5.54 (s, 2H), 6.77 (dd, J = 8.1, 2.3 Hz, 4H), 7.08 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 6.9 Hz, 2H), 7.37 (d, J = 8.1 Hz, 4H), 7.43 (d, J = 7.0 Hz, 2H), 7.46 (d, J = 2.3 Hz, 4H) 7.55 (d, J = 7.0 Hz, 2H), 7.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.2, 54.3, 111.6, 116.5, 117.4, 123.6, 123.9, 124.1, 125.1, 125.5, 141.2, 141.4, 144.9, 145.4, 146.4, 151.0, 153.9. MALDI TOF-MS: m/z 860.7 (M^+). Anal. Calcd for $C_{50}H_{26}Cl_4N_2O_4 \cdot 0.5H_2O$: C, 69.06; H, 3.13; N, 3.22. Found: C, 68.80; H, 3.00; N, 2.97.

Synthesis of 7a and 7b. Under a dry argon atmosphere, a mixture of **3** (0.29 g, 1.0 mmol), 1,5-difluoro-2,4-dinitrobenzene (0.21 g, 1.0 mmol), and anhydrous K_2CO_3 (0.42 g, 3.0 mmol) in anhydrous DMSO (25 mL) was stirred vigorously at room temperature for 1 h. The reaction mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (40 mL) and separated, and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined organic layer was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (eluent: 5:1 CH_2Cl_2/petroleum ether) to give 99 mg (22%) of **7a** (R_f = 0.54) and 68 mg (15%) of **7b** (R_f = 0.62) as white solids. **7a**. Mp > 300 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.69 (dd, J = 8.0, 2.4 Hz, 4H), 6.83 (s, 2H), 7.07 (m, 4H), 7.13 (d, J = 2.2 Hz, 4H), 7.36−7.43 (m, 8H), 8.81 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 109.2, 114.7, 115.7, 123.6, 124.0, 124.3, 125.0, 125.8, 125.9, 126.1, 135.0, 142.8, 144.3, 145.1, 147.8, 151.7, 155.2. MALDI TOF-MS: m/z 900.9 (M^+). Anal. Calcd for $C_{50}H_{26}Cl_4N_2O_4 \cdot 0.5H_2O$: C, 68.65; H,3.21; N, 6.16. Found: C, 68.55; H, 3.40; N, 6.19. **7b**. Mp > 300 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.23 (dd, J = 8.0, 2.2 Hz, 4H), 6.47 (s, 2H), 6.95−6.97 (m, 4H), 7.12 (d, J = 2.2 Hz, 4H), 7.21 (d, J = 8.0 Hz, 4H), 7.29−7.31 (m, 4H), 8.70 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 113.1, 114.4, 115.6, 123.6, 123.9, 124.5, 124.7, 125.6, 125.8, 136.6, 142.0, 143.7, 144.5, 147.4, 153.1, 155.1. MALDI TOF−MS: m/z 900.9 (M^+). Anal. Calcd for $C_{50}H_{26}Cl_4N_2O_4$: C, 69.33; H, 3.13; N, 6.22. Found: C, 69.51; H, 3.23; N, 6.37.

Synthesis of 9a and 9b (Method A). Under a dry argon atmosphere, a mixture of **3** (0.29 g, 1.0 mmol), cyanuric chloride (0.21 g, 1.0 mmol), and anhydrous K_2CO_3 (0.97 g, 3.0 mmol) in acetone (50 mL) was stirred at room temperature for 48 h. The solvent was removed, and the residue was chromatographed on a silica gel column with ethyl acetate/petroleum ether (1:5) as the eluent to give 48 mg (12%) of pure product **9a** (R_f = 0.33) and 72 mg (18%) of **9b** (R_f = 0.48). **9a**. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.28 (s, 2H), 5.41 (s, 2H), 6.78 (dd, J = 8.0, 2.1 Hz, 4H), 7.00−7.01 (m, 4H), 7.04 (d, J = 2.1 Hz, 4H), 7.28 (d, J = 8.1 Hz, 2H), 7.33−7.37 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 53.5, 116.8, 117.9, 122.7, 123.5, 124.0, 125.6, 125.6, 142.8, 144.1, 144.8, 146.2, 147.6, 171.5, 174.4. MALDI TOF-MS: m/z 795.6 (M^+). Anal. Calcd for $C_{46}H_{24}Cl_2N_6O_4$: C, 69.44; H, 3.04; N, 10.56. Found: C, 69.32; H, 3.21; N, 10.45. **9b**. Mp > 300 °C. ^{1}H NMR (600 MHz, 238K, $CDCl_3$): δ 3.97 (s, 1H), 5.46 (s, 1H), 5.80 (s, 1H), 5.88 (s, 1H), 5.94 (s, 1H), 6.84 (dd, J = 8.0, 1.9 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 7.13−7.15 (m, 2H), 7.26 (t, J = 7.3 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.51 (s, 2H), 7.53 (d, J = 7.4 Hz, 1H), 7.57 (d, J = 6.25 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.67 (s, 2H), 7.81 (d, J = 7.1 Hz, 2H). MALDI TOF−MS: m/z 795.6 (M^+). Anal. Calcd for $C_{46}H_{24}Cl_2N_6O_4$: C, 69.44; H, 3.04; N, 10.56. Found: C, 69.59; H, 3.00; N, 10.75.

Synthesis of 9a and 9b (Method B). To an ice bath cooled solution of cyanuric chloride (1.84 g, 10 mmol) in THF (50 mL) was added dropwise a mixture of **3** (1.43 g, 5 mmol) and diisopropylethylamine (1.50 g, 12.5 mmol) in THF (50 mL) during 2 h. The reaction mixture was stirred for another 2.5 h, and then filtrated. The filtrate was concentrated and chromatographed on a silica gel column (eluent: 1:3 ethyl acetate/petroleum ether) to give pure **10** (1.69 g, 58%) as a white solid. Mp: 215−216 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 5.80 (s, 1H), 5.84 (s, 1H), 6.98 (dd, J = 8.1, 2.4 Hz, 2H), 7.04−7.07 (m, 2H), 7.45 (d, J = 2.1 Hz, 2H), 7.48−7.55 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 53.4, 54.1, 118.0, 118.7, 124.8, 124.9, 125.8, 126.3, 126.5, 145.0, 145.5, 146.0, 148.3, 149.6, 172.4, 173.2. EI-MS: m/z 582 (M^+). Anal. Calcd for $C_{26}H_{12}Cl_4N_6O_2$: C, 53.64; H, 2.08; N, 14.43. Found: C, 53.47; H, 2.23; N, 14.31. To a solution of diisopropylethylamine (0.31 g, 2.4 mmol) in acetone (200 mL) were added dropwise both solutions of **3** (0.29 g, 1 mmol) in acetone (90 mL) and compound **10** (0.58 g, 1 mmol) in acetone (90 mL) at room temperature. After addition, the resulting mixture was stirred for another 48 h until the starting materials were consumed. The solvent was removed, and the residue was chromatographed on a silica gel column (eluent: 1:5 ethyl acetate/petroleum ether) to give the pure products **9a** (95 mg, 12%) and **9b** (120 mg, 15%).

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for all new compounds. X-ray crystallographic files (CIF) for compounds **5a**, **5b**, **9a**, and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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