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Synthesis, structure, and conformation of terphenylene-derived azacalix[4]aromatics

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ABSTRACT

Several novel azacalix[4]aromatics constituting terphenylene units have been synthesized via sequential nucleophilic aromatic substitution reactions of 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diamine **9** and 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)− 4,4″-diamine **11** with 1,5-difluoro-2,4-dinitrobenzene and cyanuric chloride, respectively. The bridging −NH− functions of the tetra-nitro substituted azacalix[2]arene[2]terphenylenes **1** and **2** have been transformed to the corresponding $-N(CH_3)-$ bridged azacalix[2]arene[2]terphenylenes **3** and **4** via N-alkylation. Single crystal X-ray analysis revealed that the terphenyl-3,3″-diamine derived azacalix[2]terphenylene[2]triazine **5** adopts a distorted chair conformation in the solid state, and the terphenyl-4,4″-diamine derived azacalix[2]terphenylene[2]triazine **6** was found to adopt a 1,3-alternate conformation.

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1. Introduction

Calix[*n*]arenes and their derivatives,[1] have received great research interest because of their easy synthesis, well-defined conformational and cavity structures, and the abilities to act as host molecules for wide variety of neutral or charged species. Recently, heterocalix[*n*]aromatics,[2] a class of structural analogous of calix[*n*]arenes, in which the methylene bridges of conventional calix[*n*]arenes are replaced by oxygen[3] and nitrogen[3c,4] atoms, respectively, have attracted considerable interest due to their synthetic availability, tunable cavities, and potential applications in supramolecular chemistry.[5] However, the limited number of heterocalix[*n*]aromatics available and the small cavity possessed by the heterocalix[4]aromatics family severely hampered their further use in molecular recognition and guest encapsulation. In order to improve the guest inclusion ability of the heterocalix[*n*]aromatics, two strategies have been developed to expand their cavity spaces. One was to construct heterocalix[4]aromatics with large aromatic components to enlarge their cavity spaces. For instance, the introduction of naphthyridine and naphthalene units into oxacalix[4]arene scaffold resulted in heterocalix[4]aromatics with a well-defined tweezers-like cavity separated by 7.0 Å, such a heterocalix[4]aromatic host could selectively bind *ortho*-salicylic acid in solution, and incorporate a CH_3CN molecule in the solid state.[6] The triptycene-containing heterocalix[4]aromatics developed by Chen and co-workers[7] were found to adopt fixed conformations with enlarged cavity spaces, which could encapsulate a number of different guest species. The other strategy was to introduce more aromatic rings into the heterocalix[4]aromatics scaffolds, and several larger heterocalix[*n*]aromatics [*n*>4] have thus been constructed.[3m,8] The guest complexation behaviour of some heterocalix[*n*]aromatics [*n*>4] have been evaluated.

Due to its kinked shape, *m*-terphenylene has long been used as a key strut of phenylene-based macrocycles[9] and foldamers.[10] Very recently, we[11] and others[12] have employed terphenyl-4,4″-diol in the synthesis, structural and conformational studies of oxacalix[2]terphenylene[2]aromatics. Due to the conformational flexibilities of the *m*-terphenylene units, both 1,3-alternate and chair conformations have been adopted by the oxacalix[2]terphenylene[2]aromatics.[11,12] A molecular cavity was formed by a chair conformational oxacalix[2]terphenylene[2]pyrazine, which could trap a guest molecule of ethyl acetate in the solid state.[11] However, terphenylene units have not been found in the construction of azacalixaromatics. Herein, we wish to report our recent results on the construction of several 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)- 3,3″-diamine **9** and 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-4,4″-diamine **11** derived azacalix[2]terphenylene[2]aromatics (Scheme 1). The *t*-butyl group on the *m*-phenylene units serves to increase the solubility of the resulting

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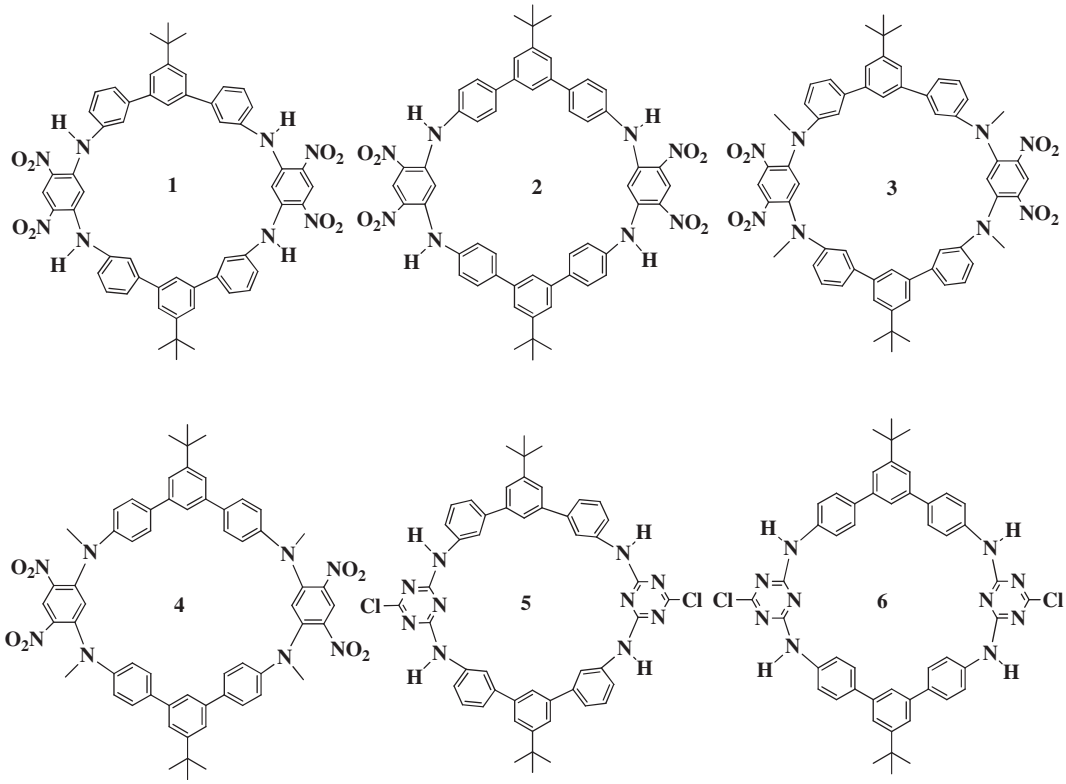
macrocycles in organic solvents. The structural and conformational properties of some resulting azacalix[2]terphenylene[2]aromatics are discussed.



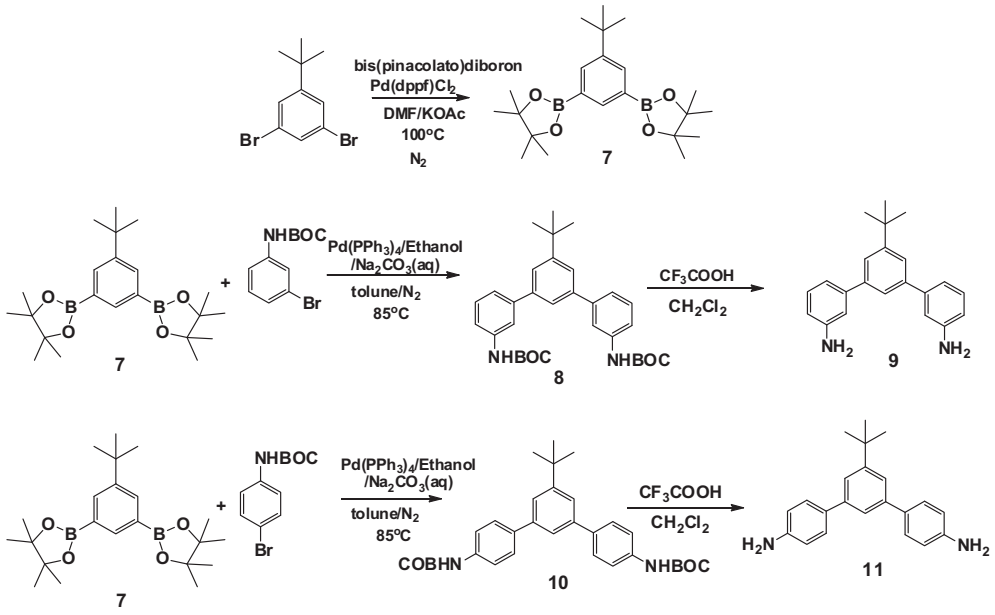
Scheme 1. The structures of the reported terphenylene-based azacalix[4]aromatics.

2. Results and discussion

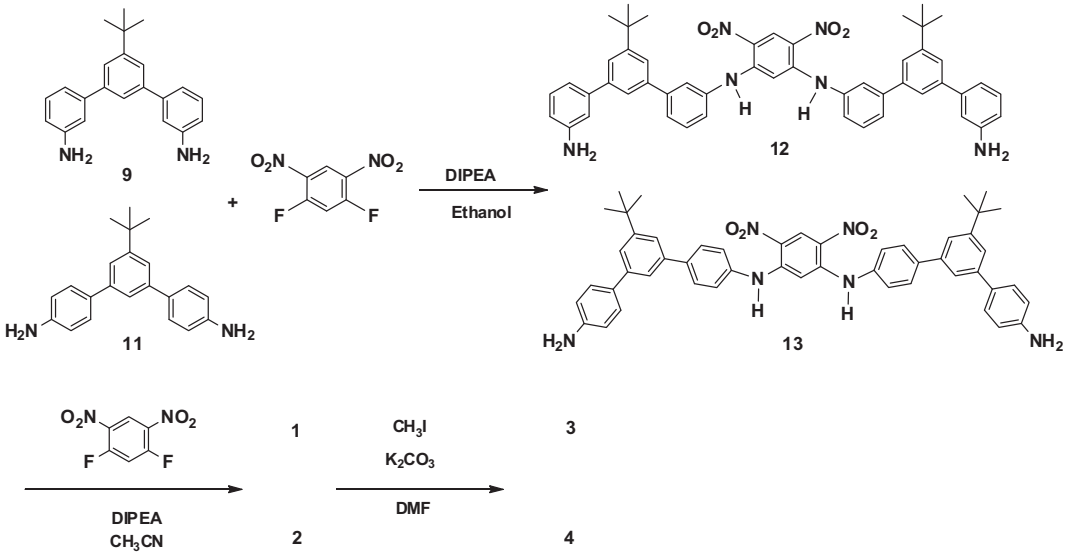
5′-*t*-Butyl-(1,1′:3′,1″-terphenyl)-3,3″-diamine **9** and 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-4,4″-diamine **11** were prepared according to a modified literature method (Scheme 2).[13] Synthesis of the terphenylene-based azacalix[4]aromatics is depicted in Schemes 3 and 4 (details see experimental section). Direct cyclo-oligomerization of **9**(**11**) with 1,5-difluoro-2,4-dinitrobenzene provided tetra-nitro substituted azacalix[2]arene[2]terphenylenes **1** and **2** in very low yields, thus, a sequential coupling strategy is employed in their synthesis. The terphenyl-diamines **9**(**11**) reacted with 1,5-difluoro-2,4-dinitrobenzene (0.5 equiv) in reflux EtOH in the presence of N(*i*-Pr)$_2$(Et) (DIPEA) for 24 h resulted in the precipitation of linear product **12**(**13**) as yellow solid, which was used directly in the next step of the synthesis. **12**(**13**) reacted with 1,5-difluoro-2,4-dinitrobenzene (1.0 equiv) in reflux CH_3CN in the presence of N(*i*-Pr)$_2$(Et) for 48 h and afforded −NH− bridged azacalix[2]arene[2]terphenylene **1**(**2**) as yellow solid(s). However, the solubility of **1** and **2** are extremely poor in almost all organic solvents, which prevented their characterization. To improve their solubility, methylation of the −NH− bridges of **1** and **2** was carried out. The tetra-nitro substituted −N(CH_3)-bridged azacalix[2]arene[2]terphenylenes **3** and **4** were thus obtained by the reaction of **1** and **2** with methyl iodide in the presence of K_2CO_3, in the overall yields of 41% and 31%, respectively, as shown in Scheme 3. No decent ^{1}H and ^{13}C NMR spectra of **1** and **2** were obtained duo to their severely low solubility. The tetra-nitro substituted −N(CH_3)− bridged azacalix[2]arene[2]terphenylenes **3** and **4** were characterized by ^{1}H, ^{13}C NMR structures of **3** and **4** are highly fluxional or different conformational structures, interchange rapidly in the NMR time scale (^{13}C NMR spectra of **3** and **4** see Supplementary data).

The terphenyl−diamine **9**(**11**) reacted with cyanuric chloride (2.2 equiv) in the presence of N(*i*-Pr)$_2$(Et) in THF at 0° resulted in linear trimer **14**(**15**), which was further reacted with **9**(**11**) (1.0 equiv) in acetone under dilute condition in the presence of N(*i*-Pr)$_2$(Et) for 72 h afforded dichloronated −NH− bridged azacalix[2]terphenylene[2]triazines **5**(**6**) as white solid(s) in the overall yield(s) of 22% (43%), as shown in Scheme 4. Dichloronated azacalix[2]terphenylene[2]triazine **5** and **6** were characterized by ^{1}H, ^{13}C NMR and mass spectroscopies, respectively. All these data support the formation of dichloronated azacalix[2]terphenylene[2]triazines **5** and **6**. The broad peaks in the ^{1}H and ^{13}C NMR spectra of **5** indicate that compound **5** might be in a restricted conformation or different conformational structures, interchange slowly in the NMR time scale (Supplementary data). However, only one set of proton and carbon signals in the corresponding ^{1}H and ^{13}C NMR spectra of **6** were observed, which indicate that compound **6** is highly fluxional in solution or different conformational structures, interchange rapidly in the NMR time scale (Supplementary data).

In order to analyze the structures and conformations of the newly synthesized terphenylene-based azacalix[4]aromatics, X-ray crystal structure analysis was carried out. Attempts to grow single crystals of **1**, **2**, **3** and **4** with X-ray diffraction quality failed. However, single crystals of **5** and **6** suitable for X-ray diffraction studies were obtained in the mixed solvent of DMSO and chloroform. The X-ray result revealed that the terphenyl-3,3″-diamine-based



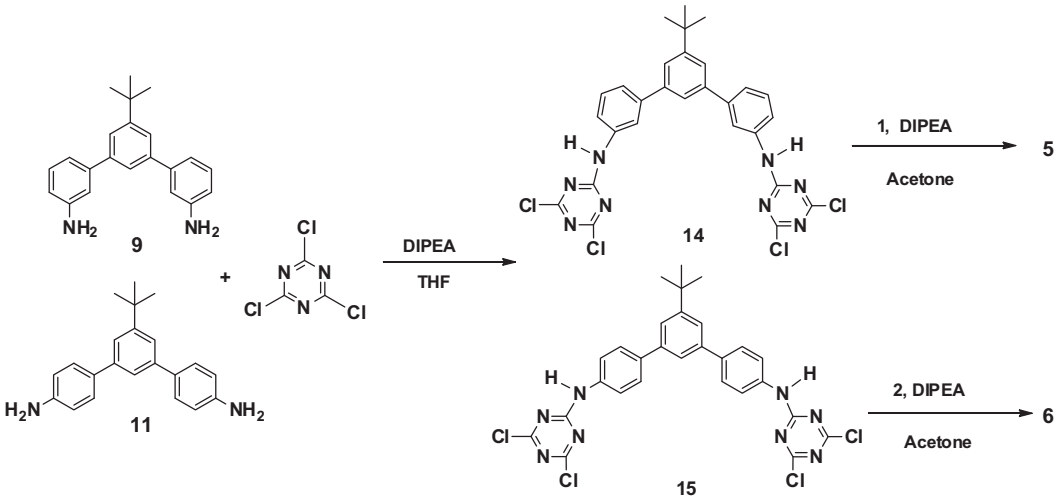
Scheme 2. Synthesis of 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diamine **9** and 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-4,4″-diamine **11**.



Scheme 3. Synthesis of tetra-nitro substituted azacalix[2]arene[2]terphenylenes **1**, **2**, **3** and **4**.

azacalix[2]terphenylene[2]triazine **5** adopts a central symmetric, twisted chair conformation in the solid state, different from the conformational structures of most literature documented azacalix[4]arenes[2] and those of the terphenylene-derived oxacalixaromatics,[11,12] as shown in Fig. 2. The pair of triazine rings is arranged eclipsing and are pointing to opposite directions with the Cl…Cl separation of 18.15 Å. The pair of terphenylene units is highly twisted. The four bridging nitrogen atoms in **5** are found located in one plane (see Fig. 2c), and form a highly symmetrical rhomboid with the two pairs of N…N distances of 4.67 Å and 10.97 Å, respectively. The bridging nitrogen atoms were found to conjugate with triazine rings (C–N bond length 1.35 Å), and no conjugation existing between the bridging nitrogen atoms and the connecting phenyl rings (C–N bond length 1.41 Å). In the crystal lattice, compound **5** are arranged in layered fashion with the interlayer space filled by solvent molecules of DMSO (Fig. 2d and e).

Due to the quality of the single crystal of **6**, we were only able to get a dataset that did not allow for high quality refinement, but could be used to confirm the basic structural motif. As show in Fig. 3, a 1,3-alternate conformation for the terphenyl-4,4″-diamine-based azacalix[2]terphenylene[2]triazine **6** is observed, similar to the conformational structures of most literature documented azacalix[4]arenes[2] and terphenylene-derived oxacalixaromatics.[11,12] The terphenylene-based azacalix[4]arene **6** adopts a 'dimeric' structure in the solid state, in which one central benzene ring plane (including its *t*-butyl substituent) of one monomer extended into the 'void' created by the two terphenylene units of the other monomer (Fig. 3). The four bridging nitrogen atoms are located in one plane. The pair of triazine rings orients to form a wide opening with a dihedral angle of 128.8°, resulting in a longer separation between the two chlorine atoms (19.94 Å). The central benzene ring planes of



Scheme 4. Synthesis of dichloronated azacalix[2]terphenylene[2]triazines **5** and **6**.

the two terphenylene units are arranged in a face-to-face manner with a dihedral angle of 72.5°, and a separation of 12.26 Å between the quaternary carbon atoms of the two *t*-butyl groups. In the solid state, large 'empty' spaces are created by the crystal packing, and are filled with highly disordered solvent molecules (DMSO). However, these solvent molecules (DMSO) are hardly to be refined due to their highly disordered nature.

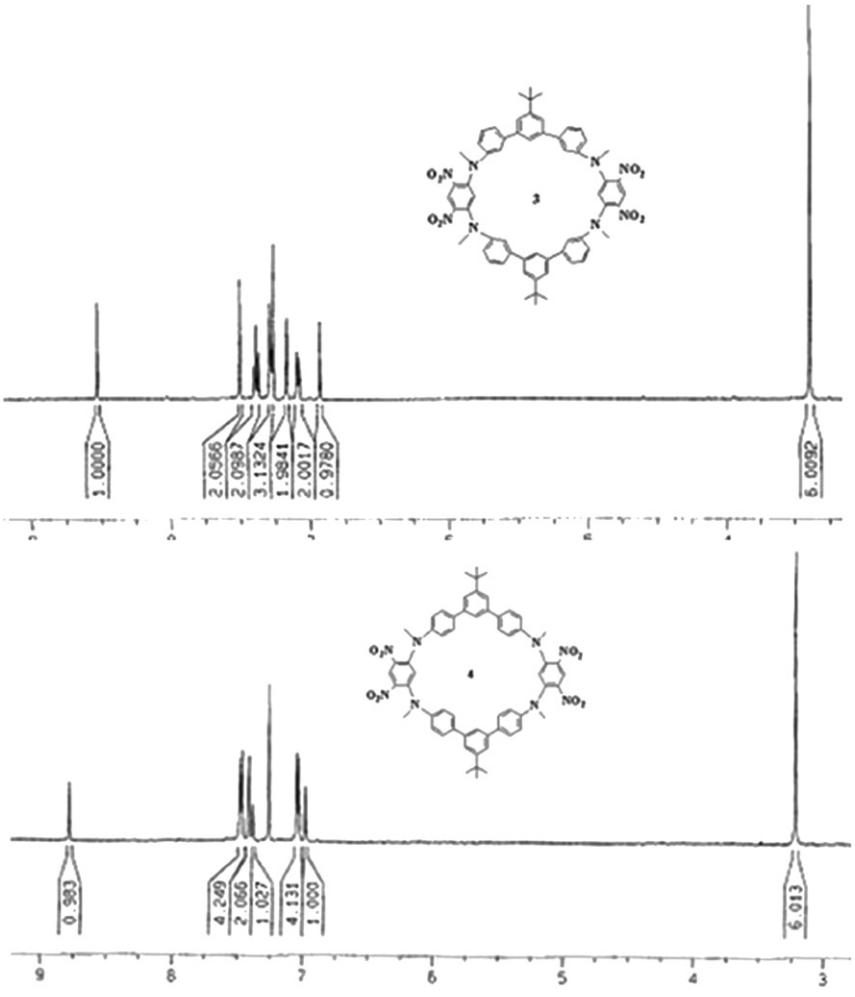


Fig. 1. ^{1}H NMR spectra of compounds **3** (top) and **4** (bottom).

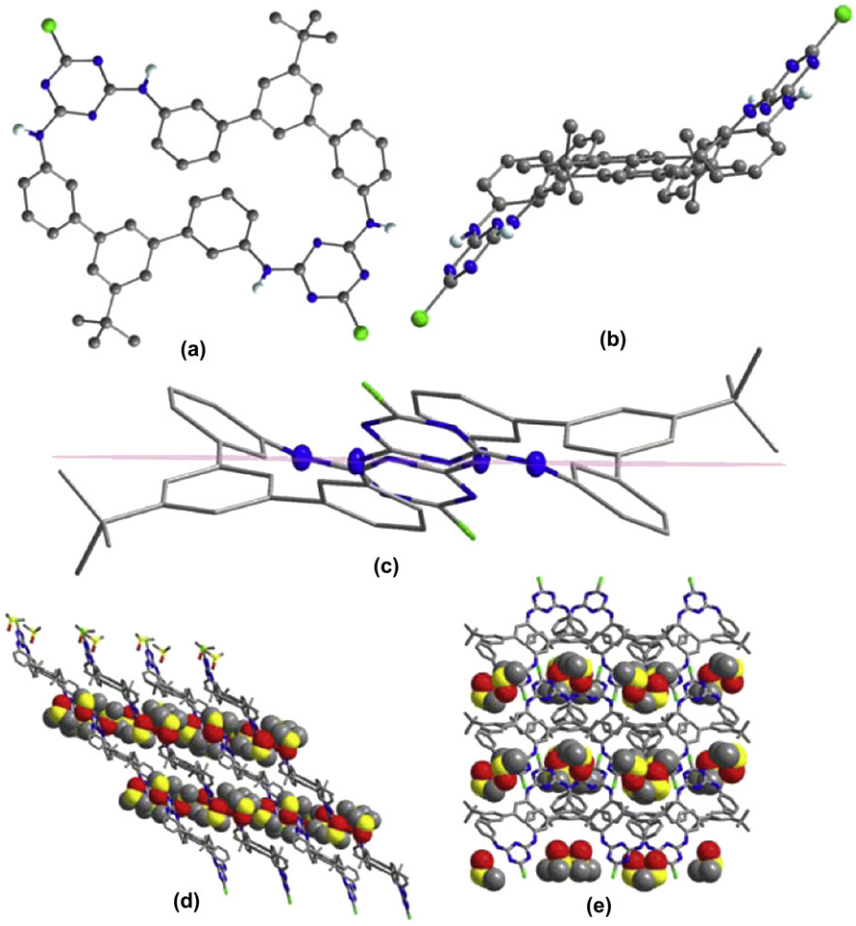


Fig. 2. Crystal structure of dichloronated azacalix[2]terphenylene[2]triazines **5** (a, top view; b, side view; c, schematic drawing of the plane formed by the four bridged nitrogen atoms) and the molecular packing (layers) in the solid state (d and e). Colour codes: oxygen=red, nitrogen=blue, chlorine=green, sulfur=yellow, carbon=gray, hydrogen=light blue.

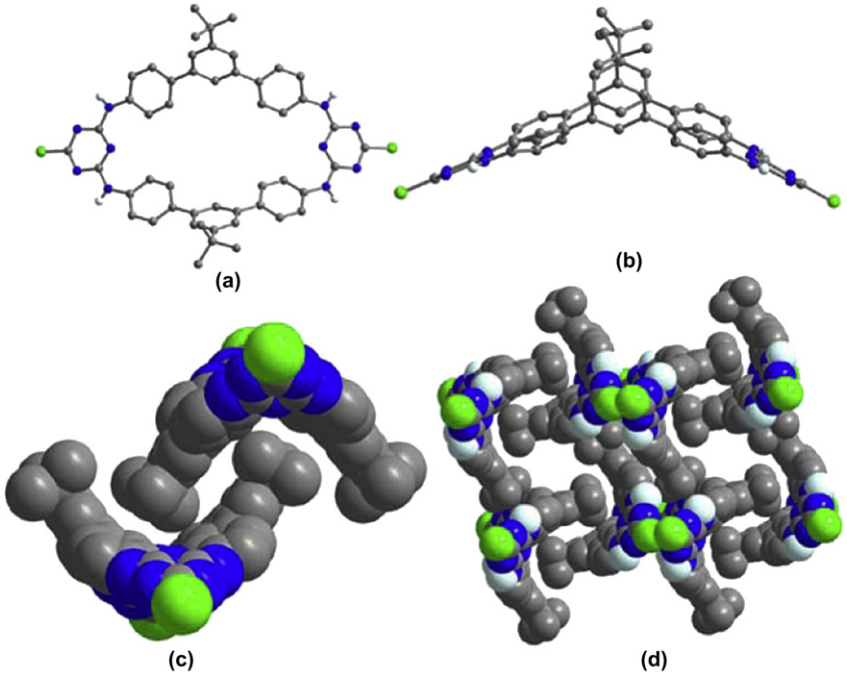


Fig. 3. Crystal structure of dichloronated azacalix[2]terphenylene[2]triazines **6** (a, top view; b, side view), the 'dimeric' structure of **6** (c) and the molecular packing in the solid state (d). Colour codes: nitrogen=blue, chlorine=green, carbon=gray, hydrogen=light blue.

3. Conclusion

In summary, we have synthesized several novel terphenylene-based azacalix[4]aromatics by aromatic S_N2 substitution reaction. Crystal structure analyses revealed that the terphenyl-3,3″-diamine **9** derived azacalixarene[2]terphenylene[2]- triazine **5** adopts a chair conformation, while the terphenyl-4,4″-diamine **11** derived azacalixarene[2]terphenylene[2]triazine **6** adopts a 1,3-alternate conformation in the solid state. No guest molecules were found to be included in the cavity spaces formed by the macrocyclic compounds **5** and **6**. Future research in this area should be focused in: (1) the design and synthesis of a family of terphenylene-derived heterocalixaromatics with a well-defined, conformation fixed and large cavity space, (2) molecular recognition and guest encapsulation abilities of such host molecules. Studies in these aspects are currently ongoing in our laboratory; the results will be reported in due course.

4. Experimental

4.1. General

Commercially available chemicals were used without further purification unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 or 400 spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the reference. Mass spectra were recorded on a microTOF QII mass spectrometer (Bruker Daltonics, Germany). Single crystal X-ray diffraction data were collected on a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ=0.71073 Å).

4.2. Synthesis of 2,2′-(5-(*tert*-butyl)-1,3-phenylene)-bis(4,4,5,5-tetramethyl- 1,3,2-dioxaborolane) 7

Potassium acetate (10.1 g, 103.2 mmol) was added to a thoroughly degassed solution of 1,3-dibromo-5-(*tert*-butyl)benzene (5.0 g, 17.2 mmol), bis(pinacolato)−diboron (10.5 g, 41.4 mmol), and [1,1′-bis(diphenylphosphino)−ferrocene] palladium dichloride (1.56 g, 2.1 mmol) in 100 mL DMF. The reaction mixture was heated at 100 °C in the nitrogen protection for 4 h. After the reaction was complete, the reaction mixture was cooled and poured into water (300 mL), and extracted with ethyl acetate (3×150 mL). The combined ethyl acetate layers were washed with water (150 mL) and brine (150 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether 100%) to give the title compound **7**. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.11 (s, 1H, Ar−H), 7.92 (d, J=0.9 Hz, 2H, Ar−H), 1.36 (s, 6H, CH_3−H), 1.34 (s, 27H, CH_3−H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 149.26, 138.74, 134.46, 83.58, 34.66, 31.43, 24.86. HRMS (ESI): m/z calcd [M+Na$^+$] $C_{22}H_{36}B_2O_4Na^+$: 409.2670; Found: 409.2609.

4.3. Synthesis of di-*tert*-butyl(5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″- diyl)dicarbamate 8

To a tolune (217 mL) solution of *tert*-butyl (3-bromophenyl)carbamate (8.5 g, 31 mmol) and 2,2′-(5-(*tert*-butyl)-1,3-phenylene) bis(4,4,5,5-tetramethyl-1,3,2- dioxaborolane) **7** (5.0 g, 13.0 mmol) was added sodium carbonate (21.2 g, 200 mmol) solution of water and ethanol (1:1, 200 mL). After the mixture was degassed and backfilled with nitrogen, $Pd(PPh_3)_4$ (1.4 g, 1.24 mmol) was added. The reaction mixture was refluxed for 30 h, and extracted with EtOAc (3×150 mL). The organic extracts were washed with brine, dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (petroleum ether/ethyl acetate 9/1) to afford di-*tert*-butyl (5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diyl)dicarbamate **8** as a white solid (4.74 g, 70.5%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.59 (d, J=1.6 Hz, 1H, Ar−H), 7.55 (s, 2H, Ar−H), 7.51 (s, 2H, Ar−H), 7.46 (s, 2H, Ar−H), 7.37 (dd, J_1=7.8 Hz, J_2=7.9 Hz, 2H, Ar−H), 7.29 (d, J=7.6 Hz, 2H, Ar−H), 6.59 (s, 2H, Ar−H), 1.53 (s, 18H, CH_3−H), 1.40 (s, 9H, CH_3−H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 152.76, 151.99, 142.66, 141.22, 138.71, 129.35, 123.62, 123.58, 122.24, 117.53, 34.95, 31.47, 28.35. HRMS (ESI): m/z calcd [M+Na$^+$] $C_{32}H_{40}N_2O_4Na^+$: 539.2880; Found: 539.2881.

4.4. Synthesis of 5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diamine 9

Di-*tert*-butyl (5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diyl) dicarbamate (1.044 g, 2.02 mmol) was dissolved in 100 mL dichloromethane, trifluoroacetic acid (6 ml) was added in portions at 0 °C. After the addition complete, the temperature was raised to rt and the reaction mixture was stirred for 24 h. The reaction mixture was then washed with 100 ml 10% NaOH (aq), dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (petroleum ether/ethyl acetate 3/1) to afford 5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diamine **9** as a yellow solid (560 mg, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.56 (d, J=1.5 Hz, 3H, Ar−H), 7.24 (dd, J_1=7.9 Hz, J_2=7.8 Hz, 2H, Ar−H), 7.04 (d, J=7.7 Hz, 2H, Ar−H), 6.96 (d, J=1.8 Hz, 2H, Ar−H), 6.70 (dd, J_1=1.5 Hz, J_2=2.1 Hz, 2H, Ar−H), 3.75 (s, 4H, NH_2−H), 1.42 (s, 9H, CH_3−H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 151.78, 146.67, 143.03, 141.51, 129.61, 123.43, 123.33, 117.87, 114.09, 114.03, 34.93, 31.47. HRMS (ESI): m/z calcd [M+Na$^+$] $C_{22}H_{24}N_2Na^+$: 317.2012; Found: 317.1993.

4.5. Synthesis of di-*tert*-butyl(5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-4,4″-diyl) dicarbamate 10

The product was obtained in a manner analogous to di-*tert*-butyl(5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diyl)dicarbamate, by employing *tert*-butyl(4-bromophenyl)carbamate (3.82 g, 14.0 mmol) and 2,2′-(5-(*tert*-butyl)-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **10** (2.66 g, 6.9 mmol) in 82.4% yield as a white solid. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 9.44 (s, 2H, NH−H), 7.63 (d, J=7.6 Hz, 4H, Ar−H), 7.56 (s, 3H, Ar−H), 7.53 (d, J=10.0 Hz, 4H, Ar−H), 1.49 (s, 18H, CH_3−H), 1.38 (s, 9H, CH_3−H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 153.31, 140.66, 139.43, 134.71, 127.39, 118.78, 79.52, 35.12, 31.57, 28.44. HRMS (ESI): m/z calcd [M+Na$^+$] $C_{32}H_{40}N_2O_4Na^+$: 539.2880; Found: 539.2914.

4.6. Synthesis of 5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-4,4″-diamine 11

The product was obtained in a manner analogous to **9** using di-*tert*-butyl (5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-4,4″-diyl)dicarbamate **10** (2.1 g, 4.06 mmol) in 97% yield as a yellow solid. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 7.41 (d, J=3.2 Hz, 3H, Ar−H), 7.37 (d, J=7.6 Hz, 4H, Ar−H), 6.65 (d, J=11.2 Hz, 4H, Ar−H), 5.18 (s, 4H, NH_2−H), 1.36 (s, 9H, CH_3−H); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm): δ 151.74, 148.68, 141.39, 128.59, 128.06, 126.45, 120.60, 114.66, 35.00, 31.75. HRMS (ESI): m/z calcd [M+Na$^+$] $C_{22}H_{24}N_2Na^+$: 317.2012; Found: 317.2090.

4.7. Synthesis of compound 3

To a EtOH (20 mL) solution of 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diamine **9** (100 mg, 0.316 mmol) and N(*i*-Pr)$_2$Et (137 μL, 0.79 mmol), was added 1,5-difluoro-2,4-dinitrobenzene (32 mg, 0.158 mmol, 0.5 equiv) at rt. After stirring at reflux for 24 h, the precipitate was isolated by filtration, followed by thorough washing

with hot water and EtOH, and dried in vacuum to afford a yellow solid **12** (86 mg crude), which was used directly in the next step. N(*i*-Pr)$_2$Et (94 μL, 0.54 mmol, 5 equiv), 1,5-difluoro-2,4-dinitrobenzene (22 mg, 0.108 mmol, 1 equiv) and **12** (86 mg, crude) were dissolved in 50 ml CH_3CN. The resulting solution was refluxed for 48 h, the precipitate was isolated by filtration, followed by thorough washing with hot water, MeCN, and EtOH to afford a yellow solid **1** (60 mg, crude). The yellow solid **1** (60 mg, crude) was dissolved in 50 ml DMF, K_2CO_3 (149 mg, 0.624 mmol), methyl iodide (31 μL, 0.5 mmol, large excess) were added in one portion. The reaction mixture was kept at 80 °C for 18 h. The mixture was then cooled and poured into water (150 mL), extracted with ethyl acetate (3×50 mL). The combined ethyl acetate layers were washed with water (50 mL) and brine (50 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (CH_2Cl_2/petroleum ether=1/1) to give the title compound **3** (65 mg, overall 41%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.53 (s, 2H, Ar–H), 7.50 (s, 4H, Ar–H), 7.38 (dd, J_1=7.8 Hz, J_2=8.0 Hz, 4H, Ar–H), 7.28 (d, J=7.3 Hz, 6H, Ar–H), 7.16 (s, 4H, Ar–H), 7.08 (dd, J_1=2.1 Hz, J_2=2.1 Hz, 4H, Ar–H), 6.93 (s, 2H, Ar–H), 3.39 (s, 12H, CH_3–H), 1.38 (s, 18H, CH_3–H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 152.37, 147.16, 146.91, 143.25, 140.90, 130.19, 127.34, 123.87, 123.56, 123.24, 119.88, 118.81, 41.46, 34.98, 31.42. HRMS (ESI): *m*/*z* calcd [M+Na$^+$] $C_{60}H_{56}N_8O_8Na^+$: 1039.4113; Found: 1039.3936.

4.8. Synthesis of compound 4

Compound **4** was obtained in a manner analogous to **3** by employing 5′-*t*-butyl-(1,1′:3′,1″-terphenyl)-4,4″-diamine **11**, instead of **9**, in 31% overall yield as a red powder. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.77 (s, 2H, Ar–H), 7.47 (d, J=8.5 Hz, 8H, Ar–H), 7.40 (s, 4H, Ar–H), 7.37 (s, 2H, Ar–H), 7.02 (d, J=8.5 Hz, 8H, Ar–H), 6.70 (s, 2H, Ar–H), 3.22 (s, 12H, Ar–H), 1.34 (s, 18H, CH_3–H); ^{13}C NMR ($CDCl_3$ and DMSO-d_6, 100 MHz, ppm): δ 151.51, 146.57, 144.55, 139.21, 136.36, 133.84, 128.24, 127.67, 125.41, 121.56, 120.69, 117.75, 34.29, 30.87. HRMS (ESI): *m*/*z* calcd [M+H$^+$] $C_{60}H_{57}N_8O_8$:1017.4294; Found: 1017.4237.

4.9. Synthesis of compound 14

To an ice-cooled THF (50 mL) solution of cyanuric chloride (385 mg, 2.089 mmol) was added a THF (50 mL) solution of diisopropyl(ethyl)amine (414 μL, 2.373 mmol) and 5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diamine **9** (300 mg, 0.949 mmol) dropwise over 1 h. The resulting mixture was stirred for additional 5 h at room temperature. After removal of diisopropyl(ethyl)amine hydrochloride by filtration, the filtrate was concentrated and chromatographed on a silica gel column (petroleum ether/EtOAc: 9:1) to give **14** as a white solid (310 mg, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.93 (s, 2H, Ar–H), 7.80 (s, 2H, Ar–H), 7.64 (s, 2H, Ar–H), 7.51 (d, J=2.0 Hz, 5H), 1.45 (s, 9H, CH_3–H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.22, 152.70, 142.76, 140.65, 136.27, 129.72, 124.66, 123.95, 123.44, 120.23, 120.03, 35.08, 31.45. HRMS (ESI): *m*/*z* calcd [M+Na$^+$] $C_{28}H_{22}Cl_4N_8Na^+$: 635.0588; Found: 635.0614.

4.10. Synthesis of compound 15

Compound **15** was obtained in a manner analogous to **14** by employing **11**, instead of **9**, in about 82% yield as a white powder. Due to the easy hydrolization of the product, no decent NMR spectrum was obtained. The product was thus used directly in the next step of the synthesis.

4.11. Synthesis of compound 5

To an acetone (100 mL) solution of diisopropylethylamine (106 μL, 0.608 mmol) was added dropwise both solutions of 5′-(*tert*-butyl)-[1,1′:3′,1″-terphenyl]-3,3″-diamine **9** (80 mg, 0.253 mmol) in acetone (50 mL) and compound **14** (155 mg, 0.253 mmol) in acetone (50 mL) at room temperature over 4 h. After the addition, the resulted mixture was stirred for another 72 h until the starting materials were consumed. The solvent was removed, and the residue was chromatographed on a silica gel column (petroleum ether/ethyl acetate 7/3) to afford **5** as a white solid (87 mg, 40%). Single crystals of **5** were obtained in DMSO-d_6. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 10.35 (s, 4H, NH–H), 7.42 (d, J=5.0 Hz, 14H, Ar–H), 6.96 (d, 8H, J=3.0 Hz, Ar–H), 1.38 (s, 18H, CH_3–H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 178.63, 167.94, 163.68, 151.55, 141.27, 140.55, 138.49, 128.52, 123.09, 122.71, 122.12, 119.27, 118.75, 34.58, 31.18. HRMS (ESI): *m*/*z* calcd [M+H$^+$] $C_{50}H_{45}Cl_2N_{10}$: 855.3240; Found: 855.3148.

4.12. Synthesis of compound 6

The product **6** was obtained in a manner analogous to **5** by employing **11**, instead of **9**, and **15** (196 mg, 0.62 mmol), to afford **6** in about 43% overall yield as a white powder. Single crystals of **6** were obtained in DMSO-d_6 and $CHCl_3$. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 10.42 (s, 4H, NH–H), 7.90 (d, J=9.0 Hz, 8H, Ar–H), 7.85 (d, J=9.0 Hz, 8H, Ar–H), 7.53 (s, 4H, Ar–H), 1.35 (s, 18H, CH_3–H); ^{13}C NMR ($CDCl_3$ and DMSO-d_6, 100 MHz, ppm): δ 167.98, 163.83, 151.67, 140.34, 137.60, 136.14, 127.11, 122.30, 122.21, 120.79, 34.45, 31.01. HRMS (ESI): *m*/*z* calcd [M+Na$^+$] $C_{50}H_{44}Cl_2N_{10}Na$: 877.3020; Found: 877.2800.

4.13. Crystallographic data for compound 5

[$C_{31}H_{40}ClN_5O_3S_3$]; Mr=662.31; monoclinic; space group $P2_1/c$; a=11.7290 (4); b=17.9527 (6); c=17.7804 (6) Å; α=90°; β=116.214 (2)°; γ=90°; V=3358.90(19) Å^3; ρ_{calcd}=1.310 gcm^{-3}; T=173 (2) K; 38,228 independent measured reflections; F^2 refinement; R_1=0.0775; wR_2=0.2109. This data was deposited in the Cambridge Crystallographic data centre, CCDC 862801.

4.14. Crystallographic data for compound 6

[$C_{50}H_{44}Cl_2N_{10}$]; Mr=855.85; triclinic; space group $P\bar{1}$; a=13.542 (6); b=15.944 (7); c=17.494 (7) Å; α=77.070 (6)°; β=77.416 (7)°; γ=87.100 (6)°; V=3593 (3) Å^3; ρ_{calcd}=0.791 gcm^{-3}; T=173 (2) K; 14,850 independent measured reflections; F^2 refinement; R_1=0.0883; wR_2=0.2316. This data was deposited in the Cambridge Crystallographic data centre, CCDC 862802.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.108. These data include MOL files and InChIKeys of the most important compounds described in this article.

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