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m-Terphenyl-3,3″-dioxo-derived oxacalixaromatics: synthesis, structure, and solvent encapsulation in the solid state

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ABSTRACT

The synthesis of oxacalix[2]terphenylene[2]aromatics with enlarged macrocyclic holes by cyclo-oligomerization reaction of 5′-*tert*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol **1** with electron-deficient dihalogenated benzene and azaheterocycles is described. The structures of the macrocycles were characterized by NMR, HRMS spectroscopic and X-ray diffraction techniques. Single crystal X-ray analysis revealed that the terphenyl-3,3″-dioxo unit incorporated in the oxacalix[4]aromatics scaffold can adopt all three possible conformations (**I**, **II**, **III**). The cis-conformational terphenyl-3,3″-dioxo (**I** and **II**) derived oxacalix[4]aromatics were found to adopt both chair and boat conformations, resulted in creation of molecular cavities capable of hosting solvent molecules of chloroform. The trans-conformational terphenyl-3,3″-dioxo (**III**) derived oxacalix[4]aromatics, however, adopt a twisted chair conformation with a narrow void space incapable of hosting any guest molecules.

1. Introduction

Identifying new macrocyclic scaffolds aiming at developing functional host molecules have been a subject of intensive research in the area of supramolecular chemistry.[1] Heterocalix[*n*]aromatics,[2] structural analogous of calix[*n*]arenes,[3] are an emerging class of macrocycles and have attracted increasing research interest over the past few years because of their potential applications in this area.[4] However, most of the current existing heterocalix[4]aromatics possess relative small cavity spaces, and their applications in molecular recognition and guest encapsulation are severely limited. Recent development in improving guest encapsulation ability of the heterocalix[*n*]aromatics is either by using large aromatic components to construct heterocalix[4]aromatics or by incorporating more aromatic rings and hetero-atom bridges in the heterocalix[*n*]aromatic ($n>4$) scaffold to enlarge their cavity spaces. For instance, Katz and co-workers[5] constructed a naphthyridine- and naphthalene-based oxacalix[4]arene with a large well-defined tweezers-like cavity for selective binding of *ortho*-salicylic acid in solution and encapsulating a CH_3CN molecule in the solid state. Chen's group successfully introduced triptycene units into the heterocalix[4]aromatics scaffold to expand their molecular cavities for encapsulating variety of different guest molecules.[6] Heterocalix[*n*]aromatics ($n>4$) comprising more than four bridging oxygen or nitrogen atoms have also been constructed by Wang, Dehaen, and others.[7] However, the conformational flexibility of these macrocycles limited their broad applications in host–guest chemistry.[8]

m-Terphenylene, which possesses a kinked shape, has been proven to be a very useful building block in the construction of phenylene-based macrocycles[9] and foldamers.[10] Very recently, our group[11] and Wang's group[12] employed *m*-terphenylene-4,4″-diol in the construction of heterocalix[4]aromatics comprising *m*-terphenylene-4,4″-dioxo units. These *m*-terphenylene-based oxacalix[4]aromatics were found conformational fluxional in solution, and can adopt both 1,3-alternate and chair conformations in the solid state. The chair conformational *m*-terphenylene-based oxacalix[4]aromatics was found to form a large molecular cavity to host small guest molecules, such as solvent molecule of ethyl acetate. We envisioned that if the conformational richer terphenylene-3,3″-diol (Scheme 1), instead of terphenyl-4,4″-diol, was used as the nucleophilic partner in the macrocyclization reactions, the resulting *m*-terphenylene-3,3″-dioxo-derived oxacalix[4]aromatics may constitute several different topologies, due to different conformations

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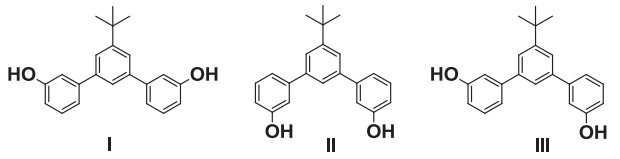
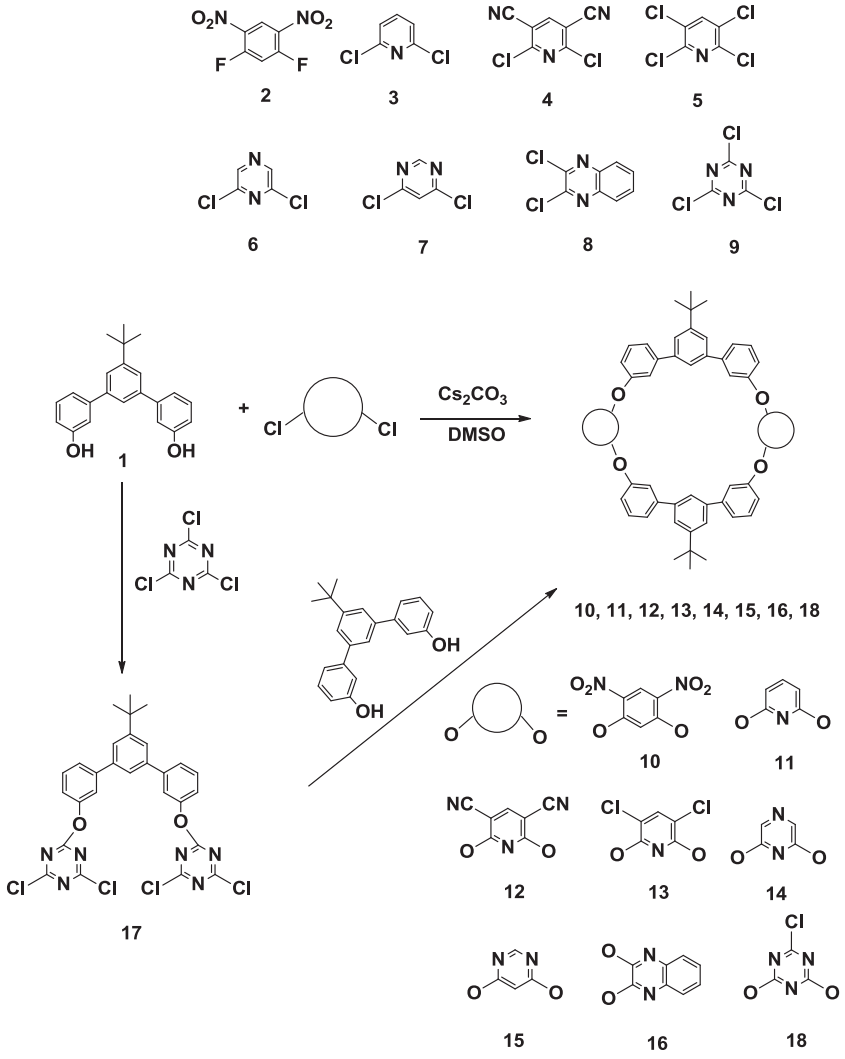


Scheme 1. Three possible conformations (cis: **I**, **II**; trans: **III**) of 5′-*tert*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol **1**.

adopted by the *m*-terphenylene-3,3″-dioxo units incorporated in these macrocycles. We have completed an efficient synthesis of *m*-terphenylene-3,3″-dioxo-derived oxacalix[4]aromatics, embedded with benzene, pyridines, pyrazines, pyrimidine, quinoxaline, and triazine, by employing 5′-*tert*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol **1** and electron-deficient *ortho*- or *meta*-dihalogenated benzene and azaheterocycles **2**–**9** as the nucleophilic and electrophilic partners, respectively, in the tetrameric cyclooligomerizatin reaction. The structures of the resulting *m*-terphenylene-3,3″-dioxo-derived oxacalix[4]aromatics were determined by elemental analysis, NMR and HRMS spectra, and single crystal X-ray diffraction studies. Single crystal X-ray analysis revealed that all three possible conformations of **1** (Scheme 1, **I**, **II**, **III**) can exist in this class of oxacalix[2]terphenylene[2]aromatics in the solid state. The oxacalix[2]terphenylene[2]aromatics embedded with cis-conformational **1** (**I**, **II**) are found to form larger molecular cavities capable of hosting small guest molecules.

2. Results and discussion

Synthesis of the *m*-terphenylene-3,3″-dioxo-based oxacalix[4]aromatics is depicted in Scheme 2 (details see Experimental section). 5′-*tert*-Butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol **1** was prepared from a modified literature method (Supplementary data).[11,13] The cyclooligomerization reaction of **1** with 1,5-difluoro-2,4-dinitrobenzene **2** in the presence of Cs_2CO_3 in DMSO at 50 °C for 3 h resulted in the formation of expected *m*-terphenylene-3,3″-dioxo-based oxacalix[4]arene **10** in the isolated yield of 90.3%. No larger *m*-terphenylene-3,3″-dioxo-based oxacalix[*n*]arenes ($n>4$) were detected.



Scheme 2. *meta*-Dihalogenated benzene and heterocycles (**2**–**9**) and the synthesis of *m*-terphenylene-3,3″-dioxo-based oxacalix[4]aromatics (**10**–**16**, **18**).

2,6-Dihalogenated pyridine electrophiles **3**–**5** were investigated to expand the structural diversity of *m*-terphenylene-3,3″-dioxo-based oxacalix[4]aromatics. Due to the low reactivity of 2,6-dichloropyridine **3**, condensation reaction of **3** with **1** in the temperature range of 50–200 °C resulted in no desired product, oxacalix[2]terphenylene[2]pyridine **11**. Fortunately, compound **11** was obtained in 27% yield by cyclocondensation reaction of **3** with **1**

in the presence of Cs_2CO_3 in DMSO at 200 °C under 50 W of microwave irradiation in 40 min. By substituting 2,6-dichloropyridine **3** with electron-withdrawing groups, such as carbonitrile (2,6-dichloropyridine-3,5-dicarbonitrile **4**) and chloride (2,3,5,6-tetrachloropyridine **5**), the electrophilicity of the resulting electrophiles (**4** and **5**) is greatly enhanced. The condensation reactions of these activated pyridine electrophiles (**4** and **5**) with **1** could thus be carried out under milder reaction conditions. The reaction of **1** with both 2,6-dichloropyridine-3,5-dicarbonitrile **4** at room temperature (2 h) and 2,3,5,6-tetrachloropyridine **5** at 200 °C (0.5 h), in the presence of Cs_2CO_3 in DMSO, furnished tetracarbonitrile-substituted oxacalix[2]terphenylene[2]pyridine **12** and tetrachlorinated oxacalix[2]terphenylene[2]pyridine **13** in 61% and 89% isolated yields, respectively. Since the product distribution of the cyclocondensation reaction is not affected by temperature and substrate concentration, the cyclic tetramers are thus believed to be thermodynamically favored products. The structural diversity of the *m*-terphenylene-3,3″-dioxo-based oxacalix[4]aromatics was further expanded by incorporating heterocyclic electrophiles, which possess two or three aromatic nitrogen atoms, such as 2,6-dichloropyrazine **6**, 4,6-dichloropyrimidine **7**, 2,6-dichloroquinoxaline **8**, and cyanuric chloride **9**. Cyclocondensation reaction of **6** with **1** in the presence of Cs_2CO_3 in DMSO at 120 °C (0.5 h) afforded oxacalix[2]terphenylene[2]pyrazine **14** in 73% yield. Analogously, compound **1** reacted with 4,6-dichloropyrimidine **7** (Cs_2CO_3, DMSO, 8 h) and 2,6-dichloroquinoxaline **8** (Cs_2CO_3, DMSO, 0.5 h) at 120 °C to afford oxacalix[2]terphenylene[2]pyrimidine **15** in 65% yield and oxacalix[2]terphenylene[2]-*o*-quinoxaline **16** in 86% isolated yield, respectively. Direct condensation reaction of cyanuric chloride **9**, which possesses three aromatic nitrogen atoms and three chloride substituents, with **1**, did not lead to the desired macrocyclic product, dichlorinated oxacalix[2]terphenylene[2]triazine **18**, possibly due to the high reactivity of **9**. By employing a fragment coupling strategy (Scheme 2), the reaction of **1** with **9** in a 1:2 ratio in THF in the presence of diisopropylethylamine (DIPEA) at 0 °C afforded the linear trimer **17** in 98% yield, and subsequent cyclocondensation reaction between **1** and **17** at room temperature in acetone, with DIPEA as a base, afforded the expected **18** in 46% isolated yield.

The structures of all the newly synthesized *m*-terphenylene-3,3″-dioxo-based oxacalix[4]aromatics **10**–**16** and **18** were established by elemental analysis, NMR and HRMS spectra. Only one set of proton and carbon signals were observed in the ^1H and ^{13}C NMR spectra of the corresponding oxacalix[2]terphenylene[2]aromatics, which indicate that the structures of these compounds are highly fluxional, or different conformational structures undergoing rapid interconversion in the NMR time scale (Supplementary data).

Most of oxacalix[4]arenes documented in the literature adopt 1,3-alternate conformations in both the solid state and solution.[2] Our previous report showed that *m*-terphenylene-based oxacalix[4]aromatics composed of *m*-terphenyl-4,4″-dioxo units can adopt both 1,3-alternate and chair conformations in the solid state.[12] In order to analyze the structures and conformations of the newly synthesized oxacalix[2]terphenylene[2]aromatics containing *m*-terphenyl-3,3″-dioxo units, single crystal X-ray structure analysis was carried out. Attempts to grow single crystals of **10**, **11**, **12**, **15**, and **18** with X-ray diffraction quality failed in all tested solvent systems. However, single crystals of **13**, **14**, and **16** suitable for X-ray diffraction studies were obtained in several different solvent systems. Single crystals of tetrachlorinated oxacalix[2]terphenylene[2]pyridine **13** were obtained in DMSO, and structure analysis revealed that **13** adopts a centrosymmetrical, highly distorted chair conformation in the solid state. The two *m*-terphenyl-3,3″-dioxo units in **13** adopt the trans-conformation **III** shown in Scheme 1. The two pyridine rings are in parallel with a transannular N···N distance of 11.02 Å. The bridging oxygen atoms are conjugated with the pyridine rings as evidenced by the short C–O bond lengths (1.34 and 1.37 Å). No conjugation exists between the oxygen atoms and the connecting phenyl rings in the *m*-terphenylene units (C–O bond lengths: 1.42 Å). The conformation adopted by the macrocycle **13** creates a narrow cavity incapable of hosting any guest molecules (Fig. 1).

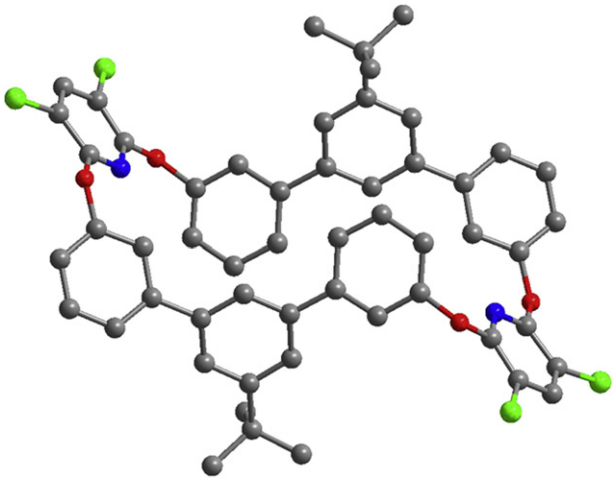


Fig. 1. Crystal structure of *m*-terphenylene-3,3″-dioxo-based tetrachlorinated oxacalix[2]terphenylene[2]pyridine **13**. Color code: C (gray), O (red), N (blue), Cl (green).

Single crystals of oxacalix[2]terphenylene[2]pyrazine **14** have been obtained in either mixed solvent of DMF and ethanol (10:1) or DMSO and chloroform (100:1). X-ray structural analysis revealed that macrocycle **14** obtained in these two solvent systems adopts two complete different conformations. As shown in Fig. 2a, **14** obtained in DMF adopts a centrosymmetrical, distorted chair conformation. The two terphenyl-3,3″-dioxo units adopt a trans-conformation **III** (Scheme 1), similar to that of **13**. The two pyrazine rings are in one plane with an intra-transannular N···N distance of 10.98 Å. No guest molecule has been found being included in the narrow void space of the molecular cavity (Fig. 2a). Shown in Fig. 2b, **14** obtained in a mixed solvent of DMSO and chloroform adopts a slightly distorted boat conformation. The two pyrazine rings are arranged in an edge-to-edge orientation with a dihedral angle of 75.8° and a centroid–centroid distance of 13.64 Å. The transannular N···N distances between the two lower rim nitrogen atoms and the two upper rim nitrogen atoms are 11.37 Å and 15.82 Å, respectively. The two terphenyl-3,3″-dioxo units adopt a cis-conformation **I** (Scheme 1), the two central benzene rings of the two terphenyl-3,3″-dioxo units tend to edge-to-edge orientation with a dihedral angle of 78.3° and a centroid–centroid distance of 8.55 Å. The conformation adopted by **14** creates a molecular cavity with a dimension of 8.55×13.64 Å, large enough to host a small guest molecule like chloroform (Fig. 2b). Since the solvent system contains only 1% percent of chloroform, the inclusion of chloroform in the macrocyclic cavity of **14** suggests that chloroform is a much more favored guest molecule than DMSO, which is dominant in the mixed solvents. In the solid state, the boat conformational **14** are arranged in stacked arrays resulting in two kinds of tubular channels, one kind is formed via aligning the macrocyclic cavities of **14** and is filled by a molecular line of chloroform guest, while the other is formed by four arrays of macrocycles **14** and is filled by two lines of chloroform molecules (Fig. 2c).

Single crystals of oxacalix[2]terphenylene[2]-*o*-quinoxaline **16** were grown in either pure DMSO or a mixed solvent of DMSO and chloroform (100:1), respectively. Crystal structure analysis revealed that different conformations were adopted by **16** obtained in these

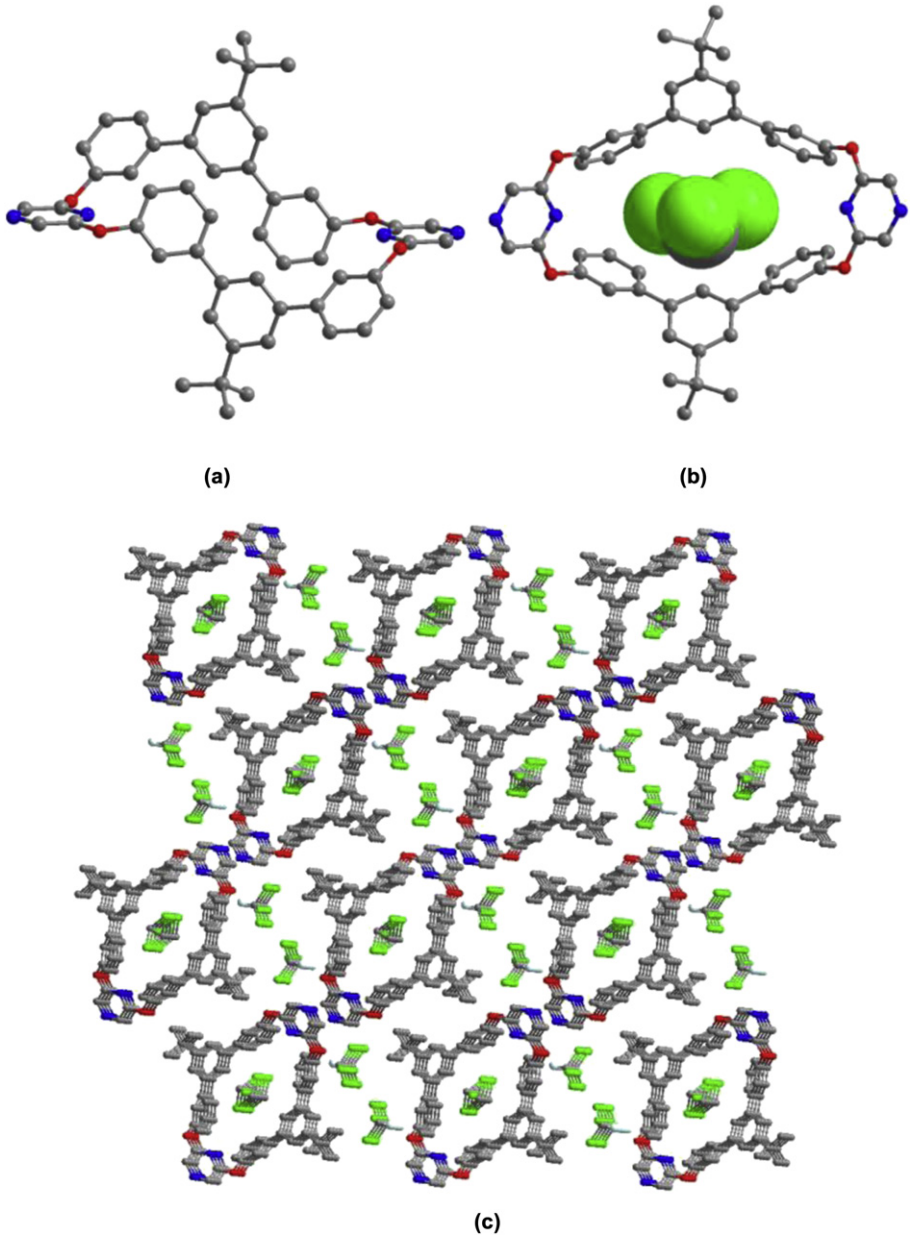


Fig. 2. Crystal structure of *m*-terphenylene-3,3″-dioxo-based oxacalix[2]-terphenylene[2]pyrazine **14** obtained in DMF and ethanol (a), and DMSO and chloroform, a chloroform guest is encapsulated in the void space of the molecular cavity (b); solid state packing for **14** obtained in DMSO and chloroform, chloroform molecules are filled in the tubular channels (c). Color code: C (gray), O (red), N (blue), Cl (green).

two solvent systems. Shown in Fig. 3, **16** obtained in DMSO adopts a centrosymmetrical, distorted chair conformation. The two terphenyl-3,3″-dioxo units adopt a cis-conformation **II** (Scheme 1) with their central phenyl rings pointing to opposite directions (Fig. 3a). The two quinoxaline planes are oriented in an *anti*-parallel configuration (Fig. 3a, b). Such an arrangement of the aromatic planes in **16** creates a molecular hole with a dimension of 7.75×7.81 Å (Fig. 3b). In the solid state, the macrocycles **16** obtained in DMSO are arranged in stacked arrays resulting in tubular channels by the alignment of the molecular holes along the *a*-axis, which are filled by guest molecules of DMSO (Fig. 3c).

Due to the quality limitation of the X-ray diffraction datasets for **16** obtained in the mixed solvent of DMSO and chloroform (100:1), we were not allowed to get a high-quality refinement, but the datasets could still allow us to determine the basic skeleton of **16**. Shown in Fig. 4, **16** obtained in the mixed solvent adopts a centrosymmetrical and slightly distorted boat conformation, possessing a boat-like geometry. In this conformation, the two face-to-face oriented *o*-quinoxaline units are eclipsing with a dihedral angle of 17.1°, and are cofacially separated by 8.60 and 9.22 Å, respectively, between the pair of pyrazinyl rings, as well as the pair of phenyl planes. The arrangement of the two *o*-quinoxaline units creates a well-defined tweezers-like cavity structure. The two terphenyl-3,3″-dioxo units also adopt the cis-conformation **II** (Scheme 1), similar to the **16** obtained in straight DMSO. The two central phenyl planes of the two terphenyl-3,3″-dioxo units bend toward the two *o*-quinoxaline units. The void space of the tweezers-like molecular cavity is found large enough to host a guest molecule of chloroform (due to its severely disordered nature, the chloroform could not be accurately refined). In the solid state, the boat conformational **16** are aligned in columns along the α-axis resulted in the formation of tubular channels. Solvent molecules of chloroform

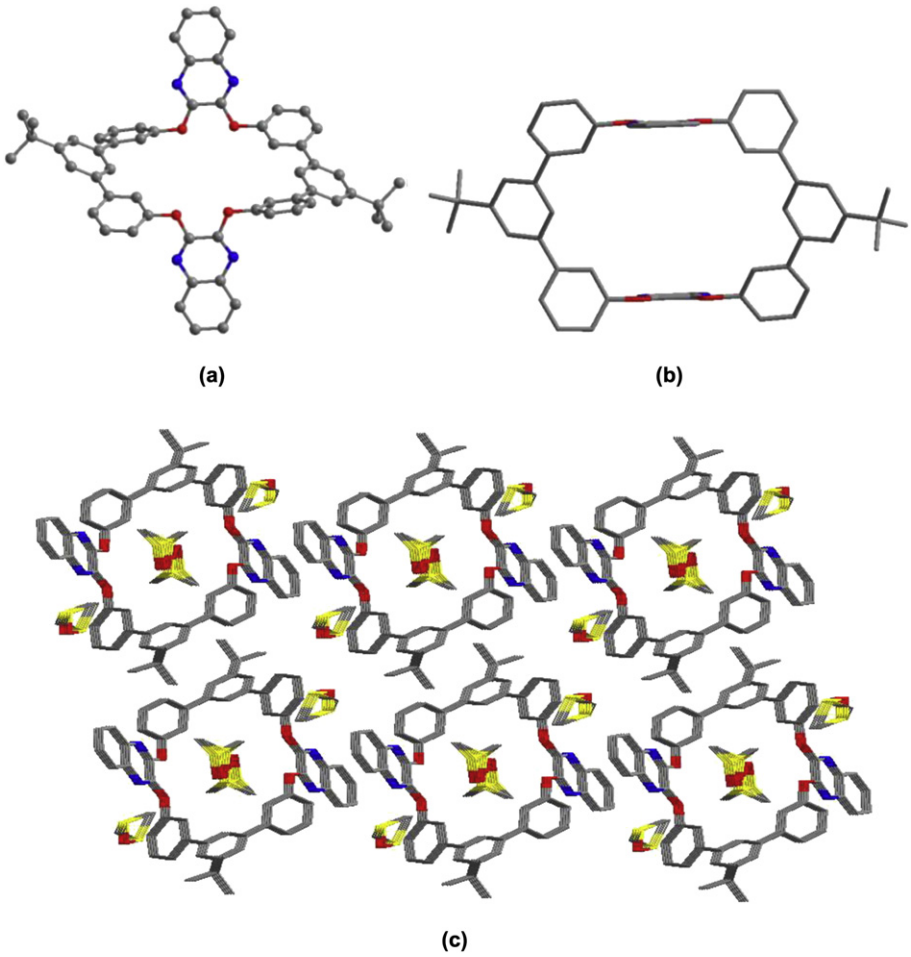


Fig. 3. Crystal structure of *m*-terphenylene-3,3″-dioxo-based oxacalix[2]-terphenylene[2]-*o*-quinoxaline **16** obtained in pure DMSO, side view (a), top view (b); solid state packing, DMSO molecules are filled in the tubular channels (c). Color code: C (gray), O (red), N (blue), S (yellow).

and DMSO are aligned alternately along the channels. Shown in Fig. 4c, chloroform molecules are also trapped in the crystal lattice.

3. Conclusions

In summary, a series of novel terphenyl-3,3″-dioxo-based oxacalix[4]aromatics have been synthesized via aromatic S_N2 substitution reaction of 5′-*tert*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol with electron-deficient *meta*-dihalogenated benzene and heterocycles. NMR spectroscopic analysis indicated that the terphenyl-3,3″-dioxo-based oxacalix[4]aromatics are conformational fluxional in solution. Single crystal X-ray data revealed that these compounds can adopt either chair or boat conformations in the solid state. The chair conformational oxacalix[2]terphenylene[2]aromatics (**13** and **14**) were found to embed two *anti*-conformational terphenyl-3,3″-dioxo units (**III**) creating a clip-like narrow space, which eliminates the possibility for hosting any guest species. However, the chair and boat conformational oxacalix[2]terphenylene[2]aromatics (**14** and **16**) were found to embed two cis-conformational terphenyl-3,3″-dioxo units (either **I** or **II**) creating large three-dimensional cavities capable of encapsulate small guest molecules such as solvent molecules of chloroform. Fixation of such topologically well-defined cavity structures possessed by the oxacalix[2]terphenylene[2]aromatics family, as well as their applications in host–guest chemistry need to be addressed in the future work. Works toward these directions are underway in our laboratory and the results will be reported in due course.

4. Experimental section

4.1. General methods

All chemicals were used as received without further purification. Chemical reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Classic column chromatography was performed using Merck 200–300 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded at Bruker Avance 500 (500 MHz) or 400 (400 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the reference. Mass spectra were recorded on a Bruker microTOF-Q spectrometer (LC/MS). Elemental analysis of new compounds was performed on an Elementar Vario EL (Germany) instrument. IR spectra were recorded on a NEXUS 670 Fourier Transform spectrometer. 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 (γ=0.71073 Å).

4.2. Synthesis of compound 10

A mixture of 5′-*tert*-butyl-(1,1′:3′,1″-terphenyl)-3,3″-diol **1** (200 mg, 0.629 mmol), 1,5-difluoro-2,4-dinitrobenzene **2** (128 mg, 0.629 mmol), and Cs_2CO_3 (452 mg, 1.386 mmol) in DMSO (100 mL) was stirred at 50 °C for 3 h. The solution was poured into 200 mL ice water, extracted with EtOAc (3×50 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/CH_2Cl_2, 1:1) to afford **10** as a pale yellow solid

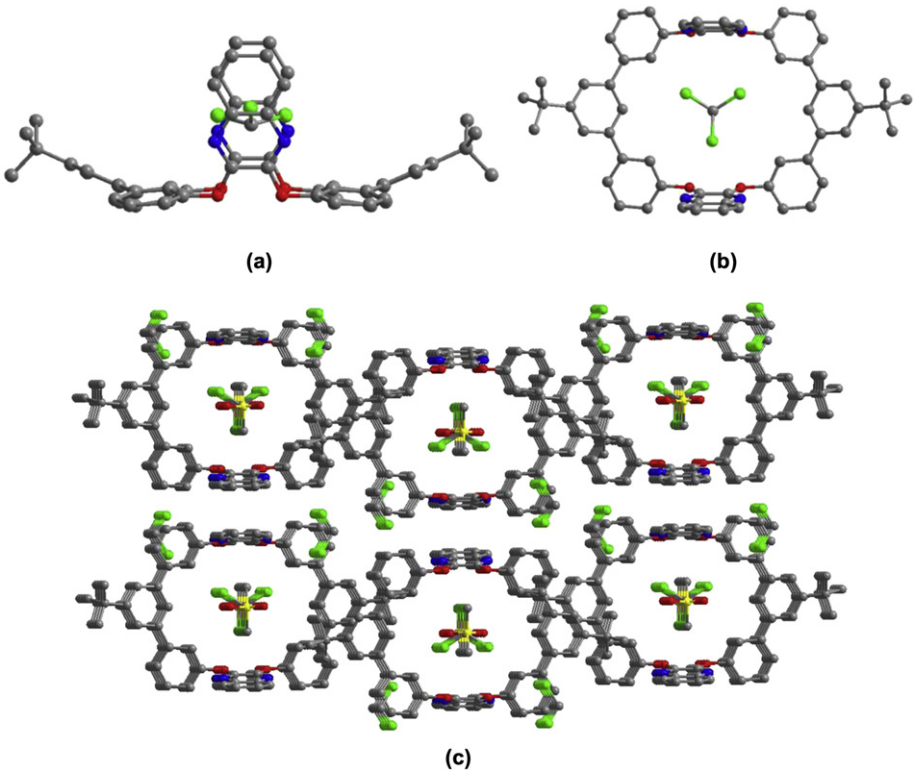


Fig. 4. Crystal structure of *m*-terphenylene-3,3″-dioxo-based oxacalix[2]-terphenylene[2]-*o*-quinoxaline **16** obtained in DMSO and chloroform (100:1), side view (a), top view (b), a chloroform guest is encapsulated in the tweezers-like cavity; solid state packing, chloroform and DMSO molecules are filled in the tubular channels (c). Color code: C (gray), O (red), N (blue), Cl (green), S (yellow).

(274 mg, 90.3%). IR (KBr): 3635.76, 2962.41, 2361.44, 1578.58, 1531.53, 1484.51, 1408.86, 1349.98, 1291.71, 1192.19, 1055.00, 840.31, 791.18, 699.20, 445.41 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 8.89 (s, 2H, Ar–H), 7.54–7.36 (m, 18H, Ar–H), 7.14 (s, 4H, Ar–H), 6.08 (s, 2H, Ar–H), 1.24 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 156.84, 153.09, 152.67, 144.05, 139.58, 132.09, 130.56, 125.68, 125.06, 123.73, 122.74, 119.66, 119.22, 105.58, 34.94, 31.35. HRMS (ESI): *m*/*z* calcd $[M+Na^+]$ $C_{56}H_{44}N_4O_{12}Na^+$: 987.2848; found: 987.2663. Anal. Calcd for $C_{56}H_{44}N_4O_{12}$: C, 69.70; H, 4.60; N, 5.81. Found: C, 70.12; H, 4.84; N, 5.92.

4.3. Synthesis of compound 11

A mixture of **1** (150 mg, 0.471 mmol), 2,6-dichloropyridine **3** (70 mg, 0.471 mmol), and Cs_2CO_3 (339 mg, 1.036 mmol) in DMSO (20 mL) in a quartz tube with a magnetic stirring bar and covered with a plastic cap. The mixture was heated at 200 °C for 40 min under 50 W of microwave irradiation. The reaction mixture was poured into 100 mL ice water, extracted with EtOAc (3×30 mL). The organic phase was washed with brine, dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (petroleum ether 100%) to afford **11** as a white solid (50 mg, 27.0%). IR (KBr): 3857.49, 3671.84, 2963.40, 2361.50, 1577.00, 1488.78, 1431.99, 1305.86, 1268.35, 1222.83, 1184.78, 1010.76, 867.14, 786.33, 698.65, 457.21 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 7.79 (dd, J_1=8.0 Hz, J_2=7.6 Hz, 2H, Py–H), 7.63 (s, 10H, Ar–H), 7.54 (d, J=7.6 Hz, 4H, Ar–H), 7.44 (dd, J_1=8.0 Hz, J_2=7.6 Hz, 4H, Ar–H), 7.14 (d, J=7.6 Hz, 4H, Ar–H), 6.54 (d, J=8.0 Hz, 4H, Py–H), 1.39 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 162.33, 153.86, 152.01, 142.82, 142.22, 140.65, 129.48, 123.45, 123.38, 120.46, 120.24, 104.00 34.97, 31.50. HRMS (ESI): *m*/*z* calcd $[M+Na^+]$ $C_{54}H_{46}N_2O_4Na^+$: 809.3350; Found: 809.3358. Anal. Calcd for $C_{54}H_{46}N_2O_4$: C, 82.42; H, 5.89; N, 3.56. Found: C, 83.05; H, 5.94; N, 3.56.

4.4. Synthesis of compound 12

A mixture of **1** (150 mg, 0.471 mmol), 2,6-dichloropyridine-3,5-dicarbonitrile **4** (93 mg, 0.471 mmol), and Cs_2CO_3 (339 mg, 1.036 mmol) in DMSO (150 mL) was stirred at room temperature for 2 h. The reaction mixture was poured into 150 mL ice water, extracted with EtOAc (3×50 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, 3:1) to afford **12** as a white solid (128 mg, 61.2%). IR (KBr): 2961.73, 2231.71, 1609.37, 1578.85, 1559.75, 1490.86, 1429.94, 1332.45, 1288.88, 1251.52, 1205.46, 1154.15, 1119.14, 922.09, 765.76, 769.80, 692.07 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 9.11 (s, 2H, Py–H), 7.36 (d, J=7.6 Hz, 8H, Ar–H), 7.29 (d, J=7.6 Hz, 4H, Ar–H), 7.18 (dd, J_1=8.0 Hz, J_2=7.6 Hz, 4H, Ar–H), 7.02 (d, J=6.0 Hz, 4H, Ar–H), 1.28 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 164.66, 152.29, 151.53, 149.47, 142.43, 139.77, 129.35, 124.77, 123.31, 122.53, 120.03, 119.74, 112.95, 90.98, 34.90, 31.44. HRMS (ESI): *m*/*z* calcd $[M+Na^+]$ $C_{58}H_{42}N_6O_4Na^+$: 909.3160; found: 909.3099. Anal. Calcd for $C_{58}H_{42}N_6O_4$: C, 78.54; H, 4.77; N, 9.47. Found: C, 77.93; H, 4.77; N, 9.20.

4.5. Synthesis of compound 13

A mixture of **1** (200 mg, 0.629 mmol), 2,3,5,6-tetrachloropyridine **5** (136 mg, 0.629 mmol), and Cs_2CO_3 (452 mg, 1.386 mmol) in DMSO (150 mL) was stirred at 120 °C for 0.5 h. The reaction mixture was poured into 200 mL ice water, extracted with EtOAc (3×100 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 **13** as a white solid (260 mg, 89.4%). Single crystals of **13** suitable for X-ray analysis were obtained from $CDCl_3$ by slow evaporation of the sample solution. IR (KBr): 3671.81,

2963.80, 1569.77, 1487.63, 1417.82, 1313.05, 1251.12, 1213.86, 1167.37, 1092.34, 943.66, 870.26, 809.93, 699.07, 457.93 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.83 (s, 2H, Py–H), 7.30 (d, J=1.1 Hz, 4H, Ar–H), 7.10 (s, 4H, Ar–H), 7.06 (d, J=6.2 Hz, 8H, Ar–H), 6.92 (s, 2H, Ar–H), 2.08 (m, 4H, Ar–H), 1.35 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 154.90, 152.87, 151.83, 142.25, 141.35, 140.21, 128.99, 123.76, 123.12, 122.79, 120.60, 120.21, 110.18, 34.87, 31.49. HRMS (ESI): m/z calcd $[M+Na^+]$ $C_{54}H_{42}Cl_4N_2O_4Na^+$: 947.1773; found: 947.2018. Anal. Calcd for $C_{54}H_{42}Cl_4N_2O_4$: C, 70.14; H, 4.58; N, 3.03. Found: C, 70.63; H, 3.76; N, 3.16.

4.6. Synthesis of compound 14

A mixture of **1** (100 mg, 0.314 mmol), 2,6-dichloropyrazine **6** (47 mg, 0.314 mmol), and Cs_2CO_3 (226 mg, 0.693 mmol) in DMSO (100 mL) was stirred at 120 °C for 0.5 h. The reaction mixture was then poured into 200 mL ice water, extracted with EtOAc (3×50 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 **14** as a white solid (90 mg, 72.6%). Single crystals of **14** were grown in either mixed solvent of DMF and EtOH (10:1) or DMSO and chloroform (100:1) by slow concentration of the sample solution. IR (KBr): 3856.55, 3064.48, 2959.68, 2363.84, 1576.76, 1532.99, 1485.58, 1403.81, 1313.43, 1253.70, 1169.70, 1043.47, 1004.38, 941.39, 864.18, 790.67, 697.97, 482.53 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.09 (s, 4H, Py–H), 7.48 (s, 4H, Ar–H), 7.28 (s, 4H, Ar–H), 7.21 (t, 9H, Ar–H), 7.01 (d, 2H, J=8.0 Hz, Ar–H), 1.41 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 157.78, 152.90, 152.20, 142.92, 140.49, 129.58, 127.01, 124.03, 123.47, 123.33, 120.33, 120.02, 34.99, 31.50. HRMS (ESI): m/z calcd $[M+Cl^-]$ $C_{52}H_{44}N_4O_4Cl^-$: 823.3046; found: 823.2902. Anal. Calcd for $C_{52}H_{44}N_4O_4\cdot H_2O$: C, 77.40; H, 5.75; N, 6.94. Found: C, 77.74; H, 6.14; N, 7.18.

4.7. Synthesis of compound 15

A mixture of **1** (100 mg, 0.314 mmol), 4,6-dichloropyrimidine **7** (47 mg, 0.314 mmol), and Cs_2CO_3 (225 mg, 0.691 mmol) in DMSO (100 mL) was stirred at 120 °C for 8 h. The reaction mixture was then poured into 200 mL ice water, extracted with EtOAc (3×50 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 **15** as a white solid (80 mg, 64.8%). IR (KBr): 3908.80, 3850.30, 3710.74, 2964.73, 2362.11, 1567.16, 1455.40, 1385.89, 1195.32, 994.80, 871.68, 700.76, 444.84 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.43 (s, 2H, Py–H), 7.63 (s, 4H, Ar–H), 7.58–7.52 (m, 10H, Ar–H), 7.42 (s, 4H, Ar–H), 7.18 (d, J=5.2 Hz, 4H, Ar–H), 6.31 (s, 2H, Ar–H), 1.42 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 171.71, 158.58, 152.64, 152.44, 143.50, 140.30, 130.30, 124.86, 123.93, 123.13, 120.72, 120.59, 91.49, 35.03, 31.45. HRMS (ESI): m/z calcd $[M+Na^+]$ $C_{52}H_{44}N_4O_4Na^+$: 811.3255; found: 811.3123. Anal. Calcd for $C_{52}H_{44}N_4O_4\cdot CH_3OH$: C, 77.54; H, 5.89; N, 6.82. Found: C, 76.66; H, 6.23; N, 6.86.

4.8. Synthesis of compound 16

A mixture of **1** (50 mg, 0.157 mmol), 2,6-dichloroquinoxaline **8** (31 mg, 0.157 mmol), and Cs_2CO_3 (113 mg, 0.346 mmol) in DMSO (100 mL) was stirred at 120 °C for 0.5 h. The solution was poured into 200 mL ice water, extracted with EtOAc (3×30 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 **16** as a white solid (60 mg, 86%). Single crystals of **16** were grown in either pure DMSO or a mixed solvent of DMSO and chloroform (100:1) by slow concentration of the sample solution. IR (KBr): 2959.87, 1742.07, 1570.16, 1493.33, 1406.42, 1373.76, 1328.66, 1240.27, 1235.77, 1198.08, 1142.19, 789.30, 755.82 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.69 (s, 4H, Ar–H), 7.65 (d, J=8.9 Hz, 6H, Ar–H), 7.59 (d, J=7.9 Hz, 4H, Ar–H), 7.55 (d, J=8.3 Hz, 5H, Ar–H), 7.49 (dd, J_1=3.35 Hz, J_2=2.85 Hz, 4H, Ar–H), 7.32 (d, J=6.55 Hz, 8H, Ar–H), 1.41 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 151.94, 151.75, 148.32, 141.95, 139.29, 129.16, 126.62, 125.90, 123.41, 122.56, 122.09, 119.88, 34.26, 30.70. HRMS (ESI): m/z calcd $[M+Na^+]$ $C_{60}H_{48}N_4O_4$ Na^+: 911.3568; Found: 911.3608. Anal. Calcd for $C_{60}H_{48}N_4O_4\cdot$DMSO: C, 76.99; H, 5.63; N, 5.79. Found: C, 77.67; H, 5.56; N, 5.66.

4.9. Synthesis of compound 17

To an ice-cooled solution of cyanuric chloride **9** (382 mg, 2.07 mmol) in THF (100 mL) was added dropwise a mixture of **1** (300 mg, 0.943 mmol) and diisopropyl(ethyl)amine (304 mg, 2.358 mmol) in THF (100 mL) over 1 h. The resulting mixture was stirred for additional 1 h. After removal of diisopropyl(ethyl)amine hydrochloride by filtration, the filtrate was concentrated and chromatographed on a silica gel column with a mixture of petroleum ether and EtOAc (100:7) as the mobile phase to give pure **17** as white solid (566 mg, 97.7%). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.60 (m, 5H, Ar–H), 7.53 (dd, J_1=8.0 Hz, J_2=7.5 Hz, 2H, Ar–H), 7.44 (s, 2H, Ar–H), 7.19 (dd, J_1=1.3 Hz, J_2=1.2 Hz), 1.43 (s, 9H, $C(CH_3)_3$–H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 173.15, 171.12, 152.74, 151.42, 143.65, 140.24, 130.24, 125.86, 124.05, 123.48, 119.83, 35.01, 31.40. HRMS (ESI): m/z calcd $[M+Na^+]$ $C_{28}H_{20}Cl_4N_6O_2Na^+$: 637.0268; found: 637.0297.

4.10. Synthesis of compound 18

To a solution of diisopropylethylamine (26 mg, 0.195 mmol) in acetone (50 mL) were added dropwise both solutions of **1** (26 mg, 0.0814 mmol) in acetone (30 mL) and compound **17** (50 mg, 0.0814 mmol) in acetone (30 mL) at room temperature. After addition, the resulting mixture was stirred for additional 96 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 100:7) to afford **18** as a white solid (32 mg, 45.8%). IR (KBr): 3777.78, 2961.90, 2362.94, 1736.12, 1547.39, 1491.45, 1447.81, 1409.68, 1366.84, 1295.66, 1261.94, 1218.92, 1180.18, 1078.53, 987.97, 872.94, 798.60, 698.39, 455.85 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.59 (s, 4H, Ar–H), 7.51 (d, J=7.6 Hz, 4H, Ar–H), 7.46–7.43 (m, 6H, Ar–H), 7.39 (s, 4H, Ar–H), 7.13 (d, J=6.9 Hz, 4H, Ar–H), 1.42 (s, 18H, $C(CH_3)_3$–H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 173.89, 172.51, 152.58, 151.65, 143.19, 140.17, 130.01, 125.23, 123.76, 123.24, 120.17, 120.06, 34.00, 31.44. HRMS (ESI): m/z calcd $[M+Na^+]$ $C_{50}H_{40}Cl_2N_6O_4Na^+$: 881.2380; found: 881.2594. Anal. Calcd for $C_{50}H_{40}Cl_2N_6O_4$: C, 69.85; H, 4.69; N, 9.77. Found: C, 69.08; H, 4.79; N, 9.54.

4.11. Crystal structure data collection and refinement

Intensity data were collected at 173(2) K or room temperature (296 K) on a diffractometer using graphite monochromated Mo Kα radiation (λ=0.71073Å). Data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97 (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Experimental data for **13**, **14**, and **16** are shown below. The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*4.11.1. Single-crystal structure of **13**.* CCDC 902748: $[C_{54}H_{42}Cl_4N_2O_4]$; M_r=924.70; T=173(2) K; triclinic; space group $P\bar{1}$; a=8.6037(17); b=10.386(2); c=12.454(2) Å; α=95.427(6)°; β=92.834(6)°; γ=94.481(6)°; V=1102.6(4) Å^3; Z=1; ρ_{calcd}=1.393 g/cm^3; crystal size=0.32×0.21×0.19 mm; μ=0.320 mm^{-1}; reflections collected 12,302; unique reflections 3815; data/restraints/parameters 3815/0/289; GOF on F^2 1.143; R_{int} for independent data 0.0438; final R_1=0.1229, wR_2=0.4071; R indices (all data) R_1=0.1410, wR_2=0.4176; largest diff. peak and hole: 1.410 and −0.637 e Å^{-3}.

*4.11.2. Single-crystal structure of **14** obtained in DMF and EtOH (10:1).* CCDC 902749: $[C_{52}H_{44}N_4O_4]$; M_r=788.91; T=173(2) K; monoclinic; space group $P2(1)/c$; a=12.3607(6); b=20.2189(9); c=8.0755(4) Å; α=γ=90°; β=93.287(2)°; V=2014.91(17) Å^3; Z=2; ρ_{calcd}=1.300 g/cm^3; crystal size=0.32×0.17×0.15 mm; μ=0.083 mm^{-1}; reflections collected 23,317; unique reflections 3551; data/restraints/parameters 3551/0/271; GOF on F^2 1.017; R_{int} for independent data 0.0636; final R_1=0.0381, wR_2=0.0805; R indices (all data) R_1=0.0646, wR_2=0.0930; largest diff. peak and hole: 0.176 and −0.179 e Å^{-3}.

*4.11.3. Single-crystal structure of **14** obtained in DMSO and chloroform (100:1).* CCDC 902750: $[C_{56}H_{46}Cl_9N_4O_4]$; M_r=1158.02; T=173(2) K; monoclinic; space group $C2/c$; a=35.508(4); b=6.0361(8); c=28.780(3) Å; α=γ=90 ; β=119.714(3) ; V=5357.3(12) Å^3; Z=4; ρ_{calcd}=1.436 g/cm^3; crystal size=0.39×0.22×0.21 mm; μ=0.521 mm^{-1}; reflections collected 29,129; unique reflections 4712; data/restraints/parameters 4712/0/330; GOF on F^2 1.074; R_{int} for independent data 0.0655; final R_1=0.0850, wR_2=0.2302; R indices (all data) R_1=0.0980, wR_2=0.2459; largest diff. peak and hole: 0.809 and −0.726 e Å^{-3}.

*4.11.4. Single-crystal structure of **16** obtained in DMSO.* CCDC 902747: $[C_{68}H_{72}N_4O_8S_4]$; M_r=1201.54; T=173(2) K; triclinic; space group $P\bar{1}$; a=8.5191(12); b=12.7920(19); c=15.089(2) Å; α=73.272(2); β=84.864(2) ; γ=81.893(2) ; V=1556.9(4) Å^3; Z=1; ρ_{calcd}=1.281 g/cm^3; crystal size=0.32×0.21×0.20 mm; μ=0.212 mm^{-1}; reflections collected 9322; unique reflections 5403; data/restraints/parameters 5403/0/408; *GOF* on F^2 1.063; R_{int} for independent data 0.0267; final R_1=0.0611, wR_2=0.1753; R indices (all data) R_1=0.0964, wR_2=0.2232; largest diff. peak and hole: 0.478 and −0.412 e Å^{-3}.

*4.11.5. Single-crystal structure of **16** obtained in DMSO and chloroform (100:1).* CCDC 902746, after solvent elimination: $[C_{60}H_{48}N_4O_4]$; M_r=889.02; T=173(2) K; monoclinic; space group $P2(1)/m$; a=9.2525(18); b=27.191(5); c=12.931(3) Å; α=γ=90°; β=106.290(3)°; V=3122.6(11) Å^3; Z=2; ρ_{calcd}=0.946 g/cm^3; crystal size=0.25×0.24×0.20 mm; μ=0.059 mm^{-1}; reflections collected 14,456; unique reflections 5599; data/restraints/parameters 4283/90/334; GOF on F^2 1.062; R_{int} for independent data 0.0440; final R_1=0.0807, wR_2=0.2420; R indices (all data) R_1=0.0990, wR_2=0.2628; largest diff. peak and hole: 0.336 and −0.299 e Å^{-3}.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.035.

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