ORIGINAL ARTICLE

Facial one-pot synthesis of D$_{3h}$ symmetric bicyclocalix[2]arene[2]triazines and their layered comb self-assembly

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Abstract A number of D$_{3h}$ symmetric bicyclocalix[2]arene[2]triazine core compounds were synthesized *via* a general and good-yielding (43–48% yield) facile protocol starting from cyanuric halides, phloroglucinol and K$_2$CO$_3$ under very mild reaction conditions. These cage-like compounds are tolerante with different reaction conditions and can be derived with other functional groups in high yields. The X-ray crystal structures show these compounds have slightly distorted D$_{3h}$ symmetric structures. Due to the unique molecular topological structure, bicyclocalix[2]arene[2]triazine molecules form unique layered comb networks when hydrogen bond groups exist (such as CO$_2$H, B(OH)$_2$), which represent a new kind of building block unit for supramolecular architectures.
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1. Introduction

Supramolecular self-assemblies, such as supramolecular cage [1] supramolecular plate [2] MOF [3] HOF [4] etc., have received great interests in the past few decades. The topological structure of the highly symmetric building-block molecule decided the architecture of the following supramolecular self-assemblies [1d,3,5]. Generally speaking, new geometric building block molecules usually bring new supramolecular architectures, and the function groups decide the way the building block molecules join each other. Most of the building blocks used at present are 2D planar molecules, building block molecules with 3D steric structures are rare.

Heteracalixaromatics are emerging supramolecular host molecule, due to their easy availability, rich structures and conformations, and powerful recognition properties [6]. They have varied 3D structures and functions and can be used as new type of building block for supramolecular architecture [7]. The cage-like heteracalixaromatics bearing enclosed cavities are particularly intriguing. Cage structure has rigid and stable configuration, it can be the ideal 3D building block unit for supramolecular architecture. The enclosed cavity of the cage also can work as a molecular flask and trap specific guest

molecules [8] stabilize the trapped species [9] and endow intrinsic porosity [10].

Up to now, the reported cage-like molecules still are few, their application in the construction of supramolecular architecture is very limited. The preparation of metal-coordinated supramolecular cages and dynamic covalent bonded cages are convenient and efficient to some extent [1,8]. But these cages usually lack stability, diversity of function groups, which limit the application of these cage molecules in supramolecular self-assemblies. The chemical stable organic cages, especially the heteracalixaromatic cages, usually were synthesized via multistep fragment coupling strategies, which is time costly and low efficient [8b,8c,11]. Katz et al. reported one case for the facile synthesis of heteracalixaromatic cage, but it can't adopt different function groups [12].

Recently, Wang et al. reported a cage-like heteracalixaromatic compound, bicyclo(tetraoxacalix[2]arene[2]triazine), synthesized from phloroglucinol and cyanuric chloride for two steps [13]. This molecule adopts a D_{3h} symmetric rigid conformation, it can be derived with nucleophilic groups such as NR_2, OR, SR. The starting materials for this cage molecule are very cheap, and very mild conditions are needed for the reaction. This molecule represents a new class of flexible scaffolds for molecular and supramolecular architecture design. However, the triazine ring is highly electron deficient, only tolerant with very limited kinds of function groups (generally electron-donating groups). By introduction of a conjugated benzene ring to the triazine ring, here we developed the heteracalixaromatic cage into a universal D_{3h} symmetric scaffold.

2. Experimental

2.1. General information

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 300M spectrometer. Chemical shifts are reported in ppm with tetramethylsilane or the residual solvent resonance as an internal standard. Melting points are uncorrected. Elemental analysis, mass spectrometry, TGA/DSC and single crystal X-ray diffraction analysis were performed on a Rigaku ST Saturn 724 + . Solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification.

2.2. The single crystal X-ray diffraction

Crystals of **2c-2e** were taken from the mother liquor and dried on a filter paper, one single crystal with proper size was loaded on the top of a glass capillary for X-ray testing. The crystal of **2f** was weathering quickly in contact with the air, single crystal of **2f** was sealed in a glass capillary with mineral oil for test.

Intensity data were collected on a Rigaku ST Saturn 724 + diffractometer equipped with a Cu target X-ray sources and an CCD detector. Crystals were cooled to 100 K (unless specified otherwise in the crystallographic data) under N_2 flow from an Oxford Cryosystems Cryostat. Data reduction was performed by a standard procedure using SAINT and empirical corrections were performed, where necessary, using SADABS. Crystal structures were solved using SHELXS-2013 by direct methods and all ordered non-hydrogen atoms were refined

anisotropically by means of fullmatrix least-squares calculations on F^2 by SHELXL-2013.

2.3. Synthesis of **3a**, **3b**, **3c** [14]

Cyanuric chloride(9.3 g, 50 mmol), anhydrous $AlCl_3$ (8.1 g, 60 mmol) and chlorobenzene (70 ml, or bromobenzene 150 °C, toluene r.t.) were added to a 250 ml single neck flask, the mixture was refluxed for 12 h until no more HCl gas released. Then, the mixture was cooled down and quenched by ice, the product was extracted by CH_2Cl_2 (60 ml*3). The extract was boiled with charcoal and evaporated by a rotating vacuum evaporator. The residue was recrystallized by the mixture of CH_2Cl_2 and petroleum ether to afford faint yellow crystal products.

3a (9.1 g, 72%): mp 148 °C; MS (ESI) m/z (%) 255.9 [M + H$^+$](1 0 0), 261.9 (95); ^1H NMR (300 MHz, CDCl$_3$) δ 8.47 (d, J = 8.6 Hz, 2H, Ar(C**H**)), 7.53 (d, J = 8.6 Hz, 2H Ar(C**H**)); ^{13}C NMR (75 MHz, CDCl$_3$) δ 173.8 (Tr(**C**)), 172.1 (Tr(**C**)), 141.4(Ar(**C**)), 131.2(Ar(C**H**)), 130.4(Ar(**C**)), 129.5(Ar(C**H**)).

3b (10.2 g, 67%): mp 165 °C; MS (ESI) m/z (%) 305.9 [M + H$^+$](1 0 0), 303.9 (62), 307.9(38); ^1H NMR (300 MHz, CDCl$_3$) δ 8.39 (d, J = 8.6 Hz, 2H Ar(C**H**)), 7.33 (d, J = 8.6 Hz, 2H Ar(C**H**)); ^{13}C NMR (75 MHz, CDCl$_3$) δ 174.0(Tr(**C**)), 172.2(Tr(**C**)), 132.5(Ar(C**H**)), 131.5(Ar(**C**)), 131.2(Ar(C**H**)), 130.3(Ar(**C**)).

3c (9.9 g, 83%): mp 146 °C; MS (ESI) m/z (%) 240.0 [M + H$^+$](1 0 0), 242.0 (63); ^1H NMR (300 MHz, CDCl$_3$) δ 8.39 (d, J = 8.4 Hz, 6H Ar(C**H**)), 7.33 (d, J = 8.4 Hz, 6H Ar(C**H**)), 2.46 (s, 3H, C**H3**); ^{13}C NMR (75 MHz, CDCl$_3$) δ 174.8(Tr(**C**)), 171.9(Tr(**C**)), 146.0(Ar(**C**)), 130.0(Ar(C**H**)), 130.0(Ar(**C**)), 129.9(Ar(C**H**)), 21.9(**C**H$_3$).

2.4. Synthesis of **2a**, **2b**, **2c**

3a (1.56 g, 6 mmol, 1.82 g for **3b**, 1.44 g for **3c**), phloroglucinol 0.25 g(2mmol), gridded K_2CO_3 (0.84 g, 6 mmol) and 50 ml acetone were added to a 50 ml single neck flask. The mixture was stirred at room temperature for 4 h, then another portion of phloroglucinol 0.25 g(2mmol), gridded K_2CO_3 (0.84 g, 6 mmol) and 50 ml acetone was added and refluxed for 2 h. After filtration, the filtrate was evaporated and the residue was recrystallized by the mixture of CH_2Cl_2 and petroleum ether to afford faint yellow crystal products.

2a (0.67 g, 46%): mp > 300 °C; MS (MALDI-TOF) m/z (%)814.0 [M + H$^+$](1 0 0), 816.0 (64),815.0 (41); ^1H NMR (300 MHz, CDCl$_3$) δ 8.54 (d, J = 8.4 Hz, 6H Ar(C**H**)), 7.55 (d, J = 8.4 Hz, 6H Ar(C**H**)), 6.78 (s, 6H, Ph(C**H**)); ^{13}C NMR (75 MHz, CDCl$_3$) δ 175.9(Tr(**C**)), 172.7(Tr(**C**)), 152.9 (Ph(**C**)), 139.8(Ar(**C**)), 132.0(Ar(**C**)), 130.2(Ar(C**H**)), 128.7(Ar(C**H**)), 114.7(Ph(C**H**)); IR (KBr) ν 2955, 1565, 1530, 1373, 1162, 1085, 1002, 815 cm^{-1}. Anal. Calcd. for $C_{39}H_{18}Cl_3N_9O_6$: C, 57.48; H, 2.23; N, 15.47. Found: C, 57.56; H, 2.31; N, 15.27.

2b (0.74 g, 43%): mp > 300 °C; MS (MALDI-TOF) m/z (%) 947.9 [M + H$^+$] (1 0 0), 949.9 (98), 950.9 (49); ^1H NMR (300 MHz, CDCl$_3$) δ 8.45 (d, J = 8.4 Hz, 6H, Ar(C**H**)), 7.71 (d, J = 8.4 Hz, 6H, Ar(C**H**)), 6.77 (s, 6H, Ph(C**H**)); ^{13}C