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Macrocycles

# Synthesis, Structure, and Properties of $O_6$-Corona[3]arene[3]tetrazines**

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**Abstract:** *$O_6$-Corona[3]arene[3]tetraazines, a new class of macrocyclic compounds, were synthesized efficiently in a one-pot reaction from the nucleophilic aromatic substitution reaction between 1,4-dihydroxybenzene derivatives and 3,6-dichlorotetrazine in warm acetonitrile. In the crystalline structure, the resulting macrocycles adopt highly symmetric structures of a regular hexagonal cavity with all bridging oxygen atoms and tetrazine rings located on the same plane with phenylene units orthogonally orientated. The constitutional aromatic rings are able to rotate around the macrocyclic annulus, depending on the steric effect of the substituents and temperature, in solution. The electron-deficient nature revealed by cyclic voltammetry, differential pulse voltammetry, and characteristic absorbances at a visible region show the $O_6$-corona[3]arene[3]tetrazines to be suitable macrocyclic receptors for electron-rich guests.*

The development of novel and functional macrocycles has been a central theme of immense scientific importance in organic and supramolecular chemistry.[1] The classic and privileged macrocyclic molecules including crown ethers,[2] cryptands,[3] spherands,[4] cyclodextrins,[5] and calixarenes[6] have provided, for instance, powerful model systems in the study of the nature of various noncovalent bond interactions, molecular recognition, and self-assembly. In addition, the functionalized macrocycles act as platforms for the fabrication of sophisticated (supra)molecular architectures, sensing systems, optoelectronic devices, and advanced materials.[1–8] Furthermore, the tailormade macrocycles serve as molecular tools, thus enabling the mechanistic study of organic reactions which involve unstable species.[9–11]

Since the beginning of the new millennium, a few fascinating synthetic macrocycles such as heteracalixaromatics,[12,13] cycloparaphenylenes,[14] and pillararenes[15] have been reported. These aesthetic molecules have been shown to be versatile synthetic receptors in supramolecular chemistry. For example, we have shown in our previous studies that the self-tunability of the electronic properties and V-shaped cavity of heteracalixaromatics originated from the interplay between the bridging heteroatoms and adjacent aromatic rings, and render the macrocycles able to interact selectively with various charged and electron-neutral guests.[12c,d] Particularly, dichloro-tetraoxacalix[2]arene[2]triazine provided a unique and powerful electron-neutral host to probe nascent noncovalent anion–π interactions.[16] To develop new macrocycles of a tunable cylindroid cavity, other than the V-shaped cleft of heteracalixaromatics, we turned our attention to coronarenes,[17] a novel class of macrocycles consisting of alternating *para*-(het)arylenes and heteroatoms. We report herein a highly efficient synthesis of unprecedented $O_6$-corona[3]arene[3]tetrazines which contain alternate phenylene and tetrazinylene units linked by oxygen atoms from a one-pot nucleophilic aromatic substitution reaction ($S_NAr$) between various 1,4-dihydroxybenzene derivatives and 3,6-dichlorotetrazine under very mild reaction conditions. The resulting macrocycles adopted unique corona-like structures of a regular hexagonal cavity in the solid state and in solution. They also showed a considerable electron-deficient nature as reflected in their photophysical and electrochemical properties, and it is crucial for the study of anion–π interactions.[18] In 1984 Franke and Vögtle[19] once reported the formation of a mixture of inseparable $O_n$-corona[$n$]arenes ($n=5$–9) in about 2% yield from the reaction of *p*-bromophenol. The hitherto known examples of structurally well-defined $O_n$-corona[$n$]arenes ($n=6$–10) were synthesized in very low overall yields, by Osakada and co-workers[20] in 2006, by means of a step-by-step preparation of oligo(*p*-phenylene oxide)s followed by cyclization through the CuI-catalyzed Ullmann coupling reaction. However, the properties of products were not investigated.

We started our study by examining the reaction between perfluoro-1,4-diphenol (**1a**) with equimolar amounts of 3,6-dichlorotetrazine (**2**), a highly electrophilic heterocyclic compound.[21] To our delight, in the presence of diisopropylethylamine (DIPEA) as an acid scavenger, **1a** reacted smoothly with **2** in warm acetonitrile to produce the fully fluorinated $O_6$-corona[3]arene[3]tetrazine compound **3a** as the sole macrocyclic product in 65% yield within 0.5 hour (entry 1, Table 1). This protocol was readily expanded to the synthesis of other $O_6$-corona[3]arene[3]tetrazines employing the 1,4-dihydroxybenzene substrates **1b**–**h**. As indicated by the results compiled in Table 1, 1,4-dihydroxybenzenes bearing 2,5-difluoro (**1b**), 2,5-dichloro (**1c**), 2,5-dibromo (**1d**), and 2,5-diester (**1e**) substituents underwent equally efficient macrocycilization reactions as **1a** with **2**, thus affording the corresponding $O_6$-corona[3]arene[3]tetrazines **3b**–**e** in good yields (entries 2–5). An excellent yield (80%) of **3f** was obtained when 2,4-dibromo-1,4-dihydroxybenzene (**1f**) was

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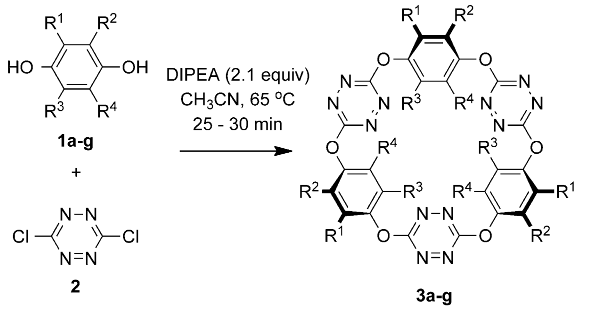
***Table 1:*** Synthesis of $O_6$-corona[3]arene[3]tetrazines **3**.[a]



| Entry | **1** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | **3** (Yield [%])[b] |
|---|---|---|---|---|---|---|
| 1 | **1a** | F | F | F | F | **3a** (65) |
| 2 | **1b** | F | H | H | F | **3b** (63) |
| 3 | **1c** | Cl | H | H | Cl | **3c** (62) |
| 4 | **1d** | Br | H | H | Br | **3d** (67)[c] |
| 5 | **1e** | $CO_2Et$ | H | H | $CO_2Et$ | **3e** (65) |
| 6 | **1f** | Br | Br | H | H | **3f** (80) |
| 7 | **1g** | H | H | H | H | **3g** (24)[d] |
| 8 | **1h** | Me | H | H | Me | **3h** (25) |

[a] The ratio of **1**/**2**/DIPEA is 1:1:2.1. [b] Yield of isolated product. [c] In a gram-scale synthesis, 75% yield was obtained. [d] Chemical yield was improved to 32% when reaction was conducted under argon protection.

reacted with **2** (entry 5). Under identical reaction conditions, 1,4-hydroquinone (**1g**) and 2,5-dimethyl-1,4-dihydroxybenzene (**1h**) reacted similarly with **2** to yield the $O_6$-corona[3]arene[3]tetrazine products **3g** (24%) and **3h** (25%), respectively (entries 7 and 8). The diminished chemical yields of **3g** and **3h** was mainly due to the oxidation of the electron-rich **1g** and **1h** to form 1,4-quinones, and the formation of insoluble linear oligomers.

The high efficiency for the synthesis of $O_6$-corona[3]arene[3]tetrazine macrocycles was remarkable. Since six new C–O bonds were formed in the construction of the $O_6$-corona[3]arene[3]tetrazines **3** from the reaction of **1** and **2**, an overall chemical yield of about 65% for **3a–e** theoretically implied that the yield for the formation of each C–O bond was nearly 93%. In the case of the production of **3f**, the yield for each individual step of C–O bond formation was as high as 97%. Although further mechanistic study is needed, formation of **3** as the major product suggested that macrocyclization was a more favorable process than oligomerization, most likely because of the thermodynamic stability of the macrocyclic product and the preorganized convergent conformation of the reactive hexameric precursors. Notably, the synthesis was readily scaled up. As a demonstration, 1.3 grams of **3d** were obtained (75% yield) when 5 mmol of the reactants **1d** and **2** were used (entry 4, Table 1).

All macrocyclic products (**3**) are crystalline compounds and gave high quality single crystals after recrystallization, thus allowing unambiguous determination of the molecular structures by X-ray crystallography. As illustrated in Figure 1 and in Figures S1–S4 in the Supporting Information, all macrocycles adopt corona-like hexagonal conformational structures in the solid state. A few interesting structural features are worth noting. First of all, all six bridging oxygen atoms in a macrocycle are located almost on the same plane with a maximum deviation of 0.29 Å. All three tetrazine rings are procumbent on the plane, while each substituted benzene ring tends to be orthogonal to the plane. For instance, the inclining angles between phenylene rings and the plane defined by bridging oxygen atoms are in the range of 69.5° to 109.2° (see Figures S1–S4), with an extreme case for **3a** in which three perfluorophenylene rings are entirely perpendicular to the plane (Figure 1a). Additionally, the linking oxygen atoms form stronger conjugation systems with their adjacent tetrazine rings than with their neighboring benzene rings. This is evidenced by the observation of shorter bond lengths between the oxygen atom and tetrazine carbon atom relative to the bond lengths between the oxygen atom and benzene carbon atom (see caption in Figure S1–S4). Furthermore, all macrocycles give an approximately regular hexagon cavity with the average bond angles around the bridging oxygen atoms in each macrocycle of 115.9°–116.5° (Figure 1b, and Figures S1–S4). Irrespective of the nature of substituents on the phenylene rings, the cavities of $O_6$-corona[3]arene[3]tetrazines have a similar size. The average distances between centroids of two proximal aromatic rings and between centroids of two distal aromatic rings are around 4.61–4.63 Å and 9.21–9.26 Å, respectively (Figure 1b,c, and Figures S1–S4). It is also interesting to point out that the three 2,5-difluorophenylene units in **3b** are oriented in such a way that fluorine atoms on one side are either positioned clockwise or

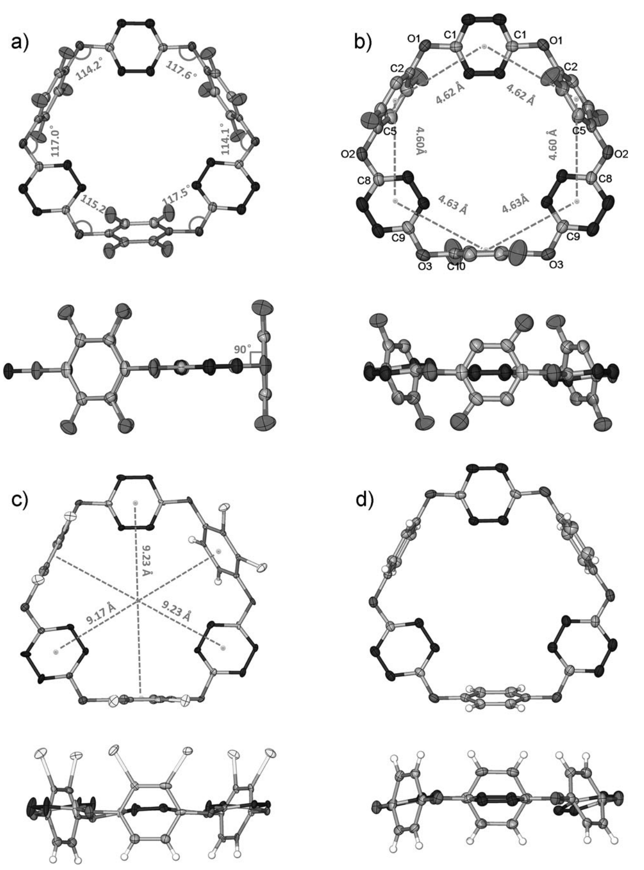


***Figure 1.*** X-ray molecular structures of **3a** (a), **3b** (b), **3d** (c), and **3g** (d) with top and side views. The solvent molecules were omitted for clarity.[27]

anticlockwise, thus yielding a $C_3$-symmetry axis (Figure 1 b). In the case of **3f**, three *o*-dibromophenylene rings point in the same direction, thus rendering the molecule a $C_{3v}$ point group (Figure 1 c).

As reflected by NMR spectroscopic data, symmetric structures of the macrocyclic $O_6$-corona[3]arene[3]tetrazines observed in the crystalline state were probably not retained in solution. For example, except for compounds **3a**, **3f**, and **3g**, which gave single sets of simple proton or fluorine and carbon signals in their $^1$H or $^{19}$F and $^{13}$C NMR spectra (see the Supporting Information), respectively, the macrocycles containing 2,5-disubstituted phenylenes showed complicated proton and carbon resonance peaks in [D$_6$]DMSO at room temperature. Upon heating to 85 °C (**3c** and **3h**; see Figures S5 and S6), to 95 °C (**3d**; Figure 2), and to 140 °C (**3e**; see Figure S7), however, the proton signals coalesced into a broad peak. Further increase of the probe temperature led to the observation of single sets of well-resolved proton and carbon signals for compounds **3c–d** and **3h** (Figure 2, and see Figures S5–S7). In the case of **3b**, a lower coalescence temperature (10 °C) was observed because of a small steric effect of the fluorine substituent (Figure S5). The outcomes of the variable-temperature NMR spectra indicated, convincingly, the presence of an equilibrium mixture of macrocyclic conformers at room temperature. Conformational isomers were able to undergo rapid interconversions at an elevated temperature, most likely through an accelerated rotation of the aromatic rings through the macrocyclic annulus on the NMR time scale. Based on variable-temperature NMR spectra, activation energies ($\Delta G^{\neq}$) were measured using a literature method.[22] An increasing order of the rotation barrier ($\mathrm{kcal\,M^{-1}}$) from 18.1 (**3c**), 18.4 (**3d**), 18.6 (**3h**) to 27.3 (**3e**; see Figures S5–S9 and Table S1) was in agreement to the increased steric hindrance of the substituents on phenylene moiety.

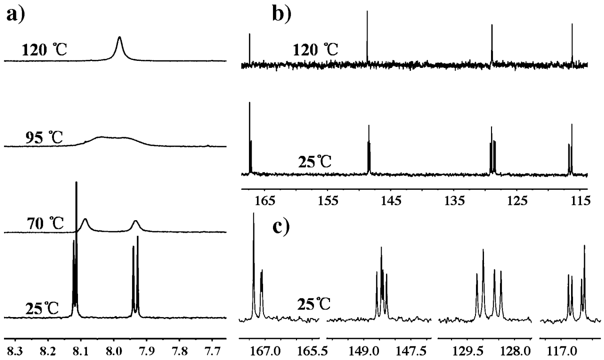


***Figure 2.*** Variable-temperature $^1$H NMR (a) and $^{13}$C NMR [b and c (expanded)] spectra of **3d** in [D$_6$]DMSO.

To understand the physicochemical properties of the $O_6$-corona[3]arene[3]tetrazines **3**, their electronic spectra and electrochemistry were investigated. For the purpose of comparison, 3,6-diphenoxy-*s*-tetrazine (**4**) was also included in the study. The UV/Vis spectra of **3** in $CH_2Cl_2$ (Figure 3) exhibited two absorption bands at $\lambda_{max} = 320–337$ nm and at $\lambda_{max} = 518–535$ nm with molar extinction coefficients ($\varepsilon$) of around $10^4\,mol^{-1}cm^{-1}$ and $10^3\,mol^{-1}cm^{-1}$, respectively (Table 2). The strong absorption bands in the short wavelength region corresponded to $\pi \rightarrow \pi^*$ transitions while the low-energy absorptions were attributable to $n \rightarrow \pi^*$ transitions of a tetrazine component.[23] Both absorption bands were shifted bathochromically with the decrease of the electron-withdrawing power of the substituents on the phenylene units. Under irradiation, **3** displayed a fluorescence emission band at $\lambda = 558–584$ nm in $CH_2Cl_2$. The emission bands were also found to be red-shifted when the electron-withdrawing ability of the substituents on the phenylene moieties was diminished. It was noteworthy that electronic spectra of **3** were highly solvent-dependent. With an increase in the polarity of the solvent, a hypochromatic rather than bathochromic shift of both absorption bands for $n \rightarrow \pi^*$ transitions and fluorescence emission bands resulted (see Figure S7–S13). The negative solvatochromism was found to correlate linearly with the $E_T(30)$ values of Reichardt's dye[23] (see Figures S17–S23).

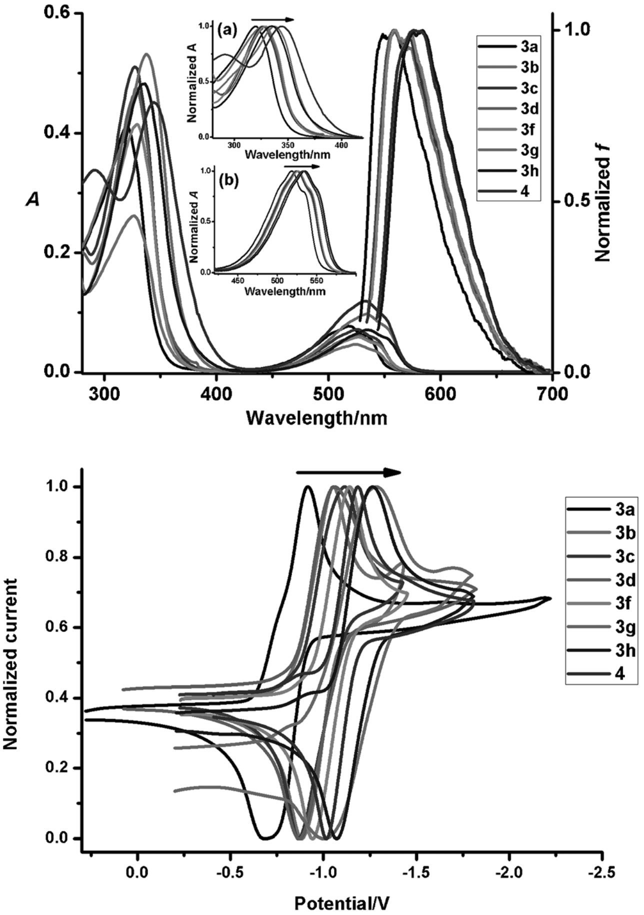


***Figure 3.*** UV/Vis spectra, normalized fluorescence spectra (top), and cyclic voltamograms (bottom) of **3a–d**, **3f–h**, and **4** in $CH_2Cl_2$ at 293 K. The insets show the normalized UV/Vis spectra from $\lambda = 280$ to 400 nm (a) and from 400 to 600 nm (b). CV measurements were carried in 0.1 M TBAP/$CH_2Cl_2$. Potentials were recorded versus $Fc^+/Fc$. The potential scan rate is 100 $mV\,s^{-1}$.

The redox properties of **3** were examined by means of cyclic voltammetry (CV) and differential pulse voltammetry

***Table 2:*** Summary of physicochemical properties of the $O_6$-corona[3]arene[3]tetrazines **3** and 3,6-diphenoxy-*s*-tetrazine (**4**).

| Entry | Compound | $\lambda_{max}$ [nm] ($\varepsilon$ [$\times 10^4$ mol$^{-1}$ cm$^{-1}$]) | $\lambda_{max}$ [nm] ($\varepsilon$ [$\times 10^4$ mol$^{-1}$ cm$^{-1}$]) | $\lambda_{ex}$ [nm] | $\lambda_{em}$ [nm] | $E_g^{opt}$ [eV][a] | $E_{1/2}$ [mV][b] | LUMO [eV][c] | HOMO [eV][d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 320 (0.94) | 518 (0.18) | 518 | 559 | 3.58 | −799 | −4.00 | −7.58 |
| 2 | **3b** | 325 (0.67) | 524 (0.12) | 525 | 558 | 3.48 | −940 | −3.86 | −7.34 |
| 3 | **3c** | 328 (1.03) | 526 (0.14) | 524 | 558 | 3.49 | −959 | −3.84 | −7.33 |
| 4 | **3d** | 328 (1.09) | 526 (0.14) | 524 | 559 | 3.49 | −942 | −3.86 | −7.35 |
| 5 | **3f** | 329 (0.95) | 526 (0.14) | 526 | 560 | 3.48 | −1003 | −3.80 | −7.28 |
| 6 | **3g** | 337 (1.25) | 534 (0.23) | 528 | 575 | 3.36 | −1135 | −3.66 | −7.02 |
| 7 | **3h** | 336 (1.20) | 535 (0.18) | 534 | 584 | 3.37 | −1131 | −3.67 | −7.04 |
| 8 | **4** | 341(0.15) | 522(0.03) | 533 | 576 | 3.31 | −1095 | −3.70 | −6.98 |

[a] $E_g^{opt} = 1240/\lambda_{abs}^{onset}$. [b] Reduction potentials measured by cyclic voltammetry with ferrocene as the standard. [c] LUMO $= -(E_{red}^{onset} + 4.8$ eV). [d] HOMO $=$ LUMO$-E_g^{opt}$.

(DPV). As depicted in Figure 3, cyclic voltammograms of **3** gave a very similar electrochemical response, thus showing a characteristic reversible redox couple resulting from one-electron reduction and oxidation of the tetrazine moiety.[24] The half-wave reduction potentials measured by CV, which are nearly identical to that obtained by means of DPV (Figure S14), are in the range of −792 mV to −1135 mV versus Fc/Fc$^+$. It appeared that the presence of stronger electron-withdrawing groups on the phenylene rings lowered the reduction potentials of the macrocycles (Table 2).

Estimated from the absorption spectra and based on reduction potentials measured electrochemically, the energy gap between LUMO and HOMO ($E_g$),[25] and both the HOMO and LUMO energy levels[26] of **3** were obtained and summarized in Table 2. It is important to point out that, in comparison to **4**, **3g** gave a red-shifted n→π* absorption band ($\Delta\lambda = 12$ nm) and a more negative reduction potential ($\Delta E_{1/2} = -40$ mV; entries 6 and 8 in Table 2). The pronounced variation of the n→π* absorption bands and reduction potentials indicated the macrocyclic effect on the photophysical and electrochemical properties of *s*-tetrazine moiety most probably because of the conformational confinement of tetrazine rings in **3**, thus resulting in the formation of stronger conjugation of a tetrazine moiety with the adjacent bridging oxygen atoms. The introduction of electron-withdrawing groups onto phenylene unit led to a decrease of the reduction potential of the tetrazine moiety (entries 1–6, Table 2). It was also noteworthy that increase of the electron-withdrawing ability of the substituents on the phenylene rings led to the decrease of both the HOMO and LUMO energy levels of the macrocycles.

In summary, we have reported the synthesis, structural characterization, and studies on the properties of a new class of macrocycles, namely, $O_6$-corona[3]arene[3]tetrazines. A one-pot nucleophilic aromatic substitution reaction between 1,4-dihydroxybenzenes and 3,6-dichlorotetrazine under very mild reaction conditions led to the formation of $O_6$-corona[3]arene[3]tetrazines efficiently. The synthesized macrocycles adopted corona-like structures with a hexagonal cavity in the crystalline state, whereas the aromatic rings were able to rotate around the macrocyclic annulus, depending on the steric effect of the substituents and temperature, in solution. The easy availability, unique conformational structures, and tunable physicochemical properties render the functionalized $O_6$-corona[3]arene[3]tetrazines useful macrocyclic receptors in many disciplines of supramolecular science. As a demonstration, **3g** behaved as an electron-deficient macrocycle to form an $[Et_4N]_3$[**3g**$Cl_3$] complex when interacting with $Et_4NCl$. The X-ray structure illustrated in Figure 4 clearly shows the formation of a typical anion–π interaction between the tetrazine ring and chloride, as each chloride is located above each tetrazine centroid at a distance of 3.06 Å–3.20 Å, which was shorter than the sum of van der Waals radii. It was also noticeable that in comparison to the parent **3g** (Figure 2d), the macrocycle in the complex was slightly twisted with the three phenylene rings being inclining to the center of the macrocycle to form weak C−H hydrogen bonds with the chlorides. A systematic study of the application of $O_6$-corona[3]arene[3]tetrazines is underway and results will be reported in due course.

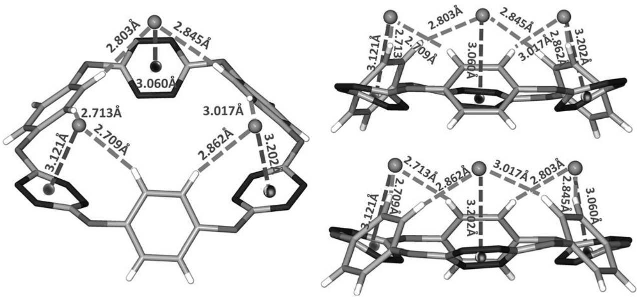


***Figure 4.*** X-ray molecular structure of $[Et_4N]_3$[**3g**$Cl_3$] with top (left) and side (right) views. Cations were omitted for clarity.[27]

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**Keywords:** anions · electrochemistry · host–guest systems · macrocycles · structure elucidation

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[17] Based on IUPAC nomenclature, the designed and synthesized macrocycles are named as 2,4,6,8,10,12-hexoxa-1,5,9(3,6)-tritetrazina-3,7,11(1,4)-tribenzacyclododecaphanes. According to the shape of macrocycles, we suggest a simple and general term corona[*n*]arenes to name macrocycles which are composed of *para*-(het)arylenes and heteroatoms in an alternative manner. While the type and the number of linking heteroatoms are prefixed to corona, the bracketed number(s) followed by the name of (het)aromatic rings after corona indicate the aromatic components. $O_6$-Corona[3]arene[3]tetrazine, for example, means a macrocycle consisting alternately of three phenylene units and three tetrazinylene units that are bridged by six oxygen atoms.

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[27] CCDC 1015930 (**3a**), 1015931 (**3b**), 1015932 (**3d**), 1015933 (**3g**), and 1015934 ($[Et_4N]_3$[**3g**$Cl_3$]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.