[Si(O2C6F4)2]14: Self-Assembly of a Giant Perfluorinated Macrocyclic Host by Low-Barrier Si−O Bond Metathesis

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Abstract: *The dynamic covalent self-assembly of 14 units of bis(perfluorocatecholato)silane leads to [Si(O2C6F4)2]14—the first giant perfluorinated macrocycle. The oligomerization process is monitored spectroscopically, and the macrocycle analyzed by single-crystal X-ray diffraction. The molecule forms a rigid cavity that can host two o-closo-dodecacarboranes. Computations rationalize the consistent and reproducible formation of the 14mer and disclose a non-catalyzed Si−O/Si−O σ-bond metathesis with an exceptionally low energetic barrier. For the first time, the most prevalent linker in our geosphere-SiO4-is disposed to construct a shape-defined crystalline macromolecule.*

Macrocyclic and spherical container molecules attract tremendous interest in all fields of chemistry.[1] They offer a multitude of applications, such as in molecular sensing, catalysis, porous materials, and many other modern nanotechnologies.[2] The spanned cavities empower nanoconfinement effects far beyond reach with top-down approaches.[3] In particular, perfluorinated hosts offer the chance to generate nanofluorous environments, acting as fluorous phase transfer catalysts or as receptors for fluorinated and chlorinated greenhouse gases.[4] However, examples of fluorinated macrocycles are scarce.[5] The sole class of perfluorinated macrocycles—medium-sized crown ethers—are accessible by low-yielding elemental fluorination only.[6] Perfluorinated macrocycles that can uptake any larger guests remain elusive. The most promising approach for the synthesis of container molecules is the self-assembly via dynamic coordinative or covalent chemistry (DCC).[7] Beyond the common DCC connections, such as imines, dynamic boron-oxygen bonds enriched the DCC toolbox more recently.[8] The Si−O bond represents yet another emerging, but much underdeveloped dynamic linker.[9] Penta- and hexacoordinated silicon anions have been applied for the construction of multi-anionic molecular squares,[10] cages,[11] and covalent organic frameworks.[12] On the other hand, catalyzed Si−O bond shuffling

within neutral silyl ethers has furnished vitrimers with remarkable thermal stabilities while maintaining self-healing features.[13] However, to the best of our knowledge, the self-assembly of well-defined molecular species via tetrahedral SiO4 units—the most prevalent building block in our geosphere—has not been described. This might result from the substantial energetic barrier for non-catalyzed Si−O σ-bond metathesis.[13d] Herewith, we report a very low-barrier version of this process, and the serendipitous discovery of a neutral macrocycle [Si(catF)2]14 (catF = O2C6F4), **1**—the first giant perfluorinated host compound.

The acetonitrile adduct of bis(perfluorocatecholato)silane, Si(catF)2·(CH3CN)2,[14] was sublimed at 250°C under 5.0×10^{-2} mbar dynamic vacuum (Figure 1). Under such conditions, the coordinated CH3CN dissociated first, as was observed by IR-spectroscopy,[14b] followed by the sublimation of putative, monomeric Si(catF)2. The white powdery sublimate dissolved in various solvents (dichloromethane, chlorobenzene, fluorobenzene, o-difluorobenzene), and the solution phase was studied by NMR spectroscopy. The 19F-NMR spectrum in CD2Cl2 showed several pairs of signals at around −158 and −163 ppm, with shifting peak integrals over a time course of several hours (Figure S2). The 29Si-NMR spectra in o-difluorobenzene or fluorobenzene revealed several peaks in the range of −100 to −104 ppm, which also were showing

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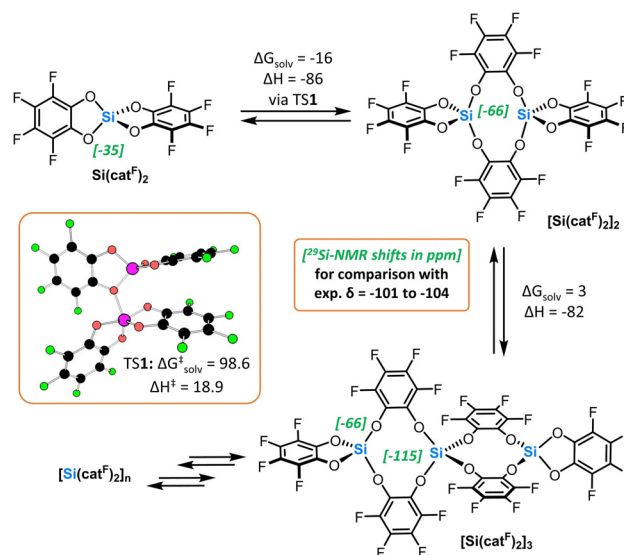https://doi.org/10.1002/anie.202009942.

Figure 1. Proposed intermediates during the formation of oligomers of Si(catF)2; computed NMR shifts (in ppm, PBE0/TZ2P), solvation corrected (COSMO-RS) Gibbs free energies (ΔGsolv) and gas-phase enthalpies of reaction (ΔH, in kJ mol⁻¹, DSD-BLYP-D3/def2-QZVPP), and transition-state structure of Si−O/Si−O σ-bond metathesis with activation parameters.

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Angew. Chem. Int. Ed. **2020**, *59*, 22510–22513

time-dependent changes (Figure S3). To get insight into the nature of those fleeting compounds, ^{29}Si-NMR shifts of potential intermediates were computed by density functional theory (see SI). The experimentally observed chemical shifts were neither in agreement with the computed chemical shift of donor-free $Si(cat^F)_2$ (-34.7 ppm) nor with that of *trans*-$Si(cat^F)_2 \cdot (CH_3CN)_2$ (-136.9 ppm). Self-aggregation by *dative* interactions two $Si(cat^F)_2$ or Lewis adducts with the fluorinated solvents was ruled out by unfavorable computed thermodynamics (see SI). In contrast, the reaction enthalpies of *covalent* oligomerization of $Si(cat^F)_2$ were computed as favorable, with almost thermoneutral Gibbs free energies in solution (Figure 1). Indeed, the experimentally observed ^{29}Si-chemical shifts agreed best with the computed values for the internal silicon atoms such as in **[Si(cat^F)_2]_3**, formed by *covalent* trimerization, or higher oligomers (Figure 1).

^{19}F DOSY-NMR on the solution phase samples of the sublimate revealed species with substantially larger solvodynamic radii as those of distinct monomeric forms (see SI). Intriguingly, the transition state energy for the dimerization of two units of $Si(cat^F)_2$ amounts to only $\Delta H^{\ddagger} = 19$ kJ mol^{-1}/ $\Delta G^{\ddagger} = 99$ kJ mol^{-1} (TS**1**, Figure 1). This is an exceptionally low barrier and represents a hitherto unprecedented spontaneous, non-catalyzed Si$-$O σ-bond metathesis.[13d] The pentacoordinate transition state is stabilized by the high Lewis acidity of the monomers, facilitating rapid chain-growth and exchange.[14] Hence, all spectroscopic and theoretical findings strongly suggested different oligomeric fragments of composition **[Si(cat^F)_2]_n** under the approach to equilibrium at the given conditions (Figure 1). Storing the solutions of the sublimate in various solvents led to the crystallization of a compound **1**, cocrystallized with disordered solvent molecules. Single-crystal X-ray diffraction of the colorless crystals obtained from a fluorobenzene solution revealed a C_{2h} symmetric macrocycle, **1**∩$(C_6H_5F)_5$, composed of 14 monomeric units of $Si(cat^F)_2$ (Figure 2).

The cavity of roughly 17 Å × 15 Å hosts three molecules of fluorobenzene. Interestingly, the rims of the barrel-shaped container are capped with two additional fluorobenzenes, potentially trapped by hydrogen bonding with the fluoride atoms of the host. This motif could indicate a templating effect during the formation process of the macrocycle from the oligomeric building blocks. However, the *14mer* was obtained reproducibly and irrespective of the chosen solvent (dichloromethane, chlorobenzene, fluorobenzene, *o*-difluorobenzene, see SI). Next, the sublimate was dissolved in the presence of icosahedral *o*-closo-dodecacarborane 1,2-$C_2B_{10}H_{12}$, forming a 1:2-host-guest-complex of **1** with the carborane (Figure 3).

The 1:2 stoichiometry nicely illustrated the large cavity size of **1**, if compared with the 1:1 dodecacarboranes complexes which form with β- and γ-cyclodextrins.[15] Poor solubility of all crystalline materials of **1**(guest)$_n$ prevented further solution-phase analyses, guest replacements, or determinations of binding constants thus far. To understand the preferred composition of the macrocycle by exclusively 14 monomeric units, all possible cyclic and acyclic oligomers **[Si(cat^F)_2]_n** ($n = 3$–20) were screened theoretically (GFN-xTB, for details, see SI).[16] For species with
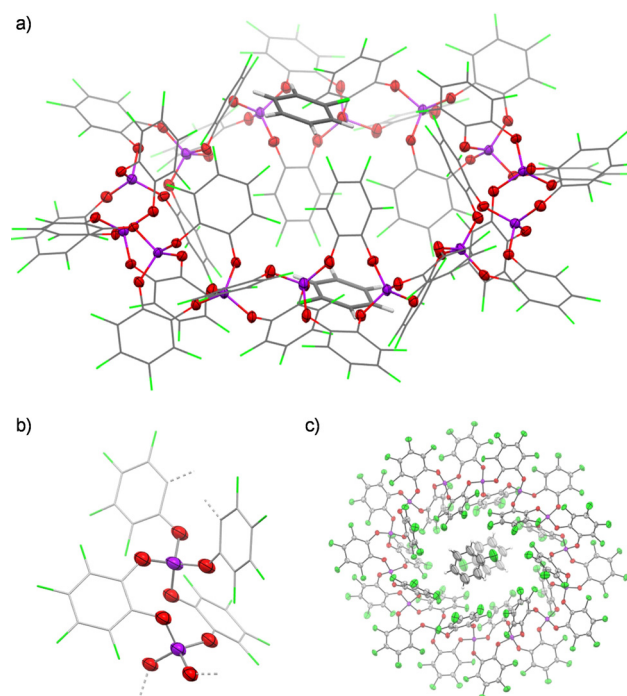
Figure 2. Single-crystal X-ray diffraction derived molecular structure of **1**∩$(C_6H_5F)_5$. **a)** Side-view, emphasizing the silicon-oxygen connectivity; **b)** Cutout depicting the tetrahedral coordination environment of two Si-centers; **c)** Top-view of the whole molecule; ellipsoids at 50% probability level; all solvent molecules except from those at the rim-region are omitted for clarity. CCDC numbers are given in the Supporting Information.
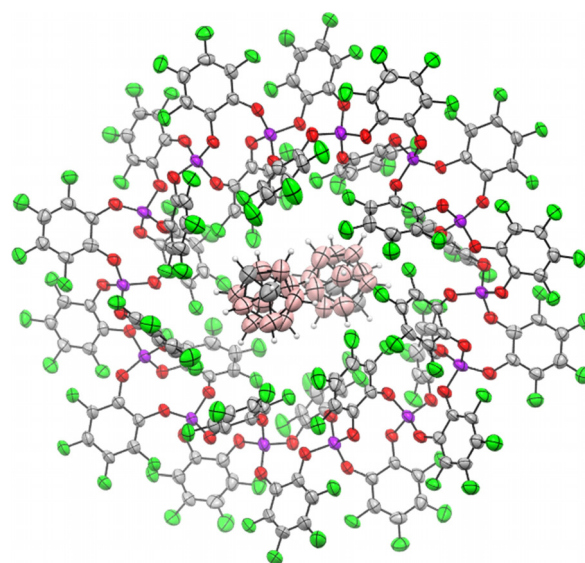
Figure 3. Single-crystal X-ray diffraction derived molecular structure of **1**∩$(1,2$-$C_2B_{10}H_{12})_2$. Thermal ellipsoids at 50% probability level. Cocrystallized solvent (pentane) and additional 1,2-$C_2B_{10}H_{12}$ molecules at the outside of the ring have been omitted for clarity. CCDC numbers are given in the Supporting Information.

$n > 6$, the cyclic form **cy-[Si(cat^F)_2]_n** with two bridging catecholates are the most stable constitutional isomers (Figure 4a and S8).
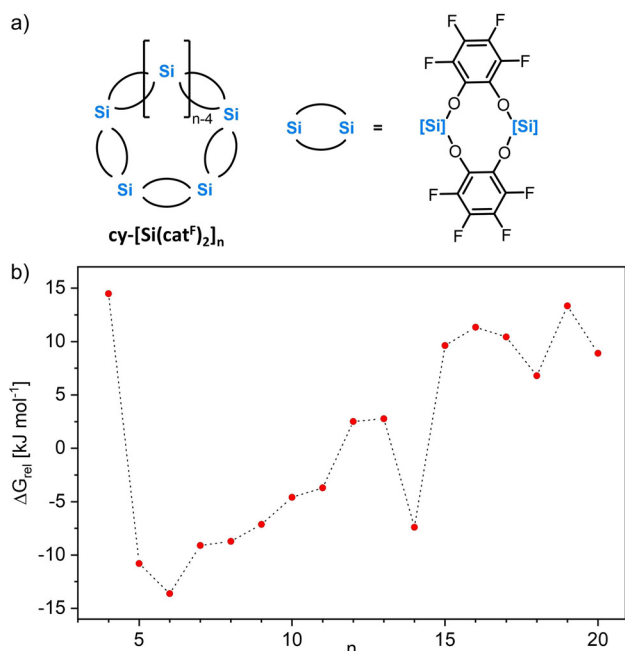
a)

b)

Figure 4. a) Thermodynamically preferred bridging modes of $[Si(cat^F)_2]_n$ for $n > 6$; b) Computed Gibbs free energies for $n\,Si(cat^F)_2 \rightarrow$ cy-$[Si(cat^F)_2]_n$ divided by n (obtained at PW6B95-D3/def2-TZVPP//HF-3c level of theory, thermal correction obtained from GFN1-xTB).

Hence, the macrocyclic structures **cy-$[Si(cat^F)_2]_n$** ($n = 4$–20) were reoptimized (HF-3c)[17] and the enthalpies of reaction for $n\,Si(cat^F)_2 \rightarrow$ **cy-$[Si(cat^F)_2]_n$** (PW6B95-D3/def2-TZVPP) divided by n, providing the normalized reaction Gibbs free energy per monomeric unit, ΔG_{rel} (Figure 4b). Much to our delight, a significant energetic slump was obtained for $n = 14$, supporting the experimental finding and a preference for this particular ring size. Potentially, the *14mer* experiences the ideal balance between ring strain and intramolecular, fluorophilic dispersion interaction.[18] The non-observability of the ring-sizes of $n = 6$–8, despite favorable computed Gibbs free-energy, is likely explained by the neglected enthalpic and entropic contribution of the solvent, which is less pronounced for larger voids.[19] Anyhow, it encourages the search of different isomers under adapted reaction conditions.

In conclusion, we describe the first spontaneous dynamic covalent self-assembly via neutral SiO_4 linkers. The process delivers a unique perfluorinated giant macrocycle as the thermodynamic product. The rigid cavity is either filled with solvent molecules or capable of uptaking two *o*-dodecacarboranes. As the silicon centers in the macrocycle remain Lewis acidic,[14] the compound potentially leverages new forms of molecular recognition or nanoconfined catalysis by action as polytopic Lewis acid. The low barrier Si-O/Si-O exchange sheds new light on our understanding of silicon ester dynamic covalent chemistry and the unique role of natural catechols in silica biomineralization.[20] It promotes the development of high-efficiency self-healing silicones[13] or even allows to consider rapid constitutional exchange in zeolites.[21]

Conflict of interest

The authors declare no conflict of interest.

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