Supporting Information

\[ \text{[Si(O}_2\text{C}_6\text{F}_4)_2]_{14}: \text{Self-Assembly of a Giant Perfluorinated Macroyclic Host by Low-Barrier Si–O Bond Metathesis} \]

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1. Materials and Methods

Unless stated otherwise, all manipulations were carried out under a dry argon atmosphere by using standard Schlenk techniques to prevent oxidation and hydrolysis of the sensitive compounds. All solvents were rigorously dried by applying standard procedures, freshly degassed and stored over molecular sieve (3 Å resp. 4 Å) prior to use. All glassware, syringes, magnetic stirring bars and needles were thoroughly dried. The commercially available chemicals were used as received.

Bis acetonitrile adduct Si(cat\(^\text{F}\)\(_2\)·(CH\(_3\)CN)\(_2\) (cat\(^\text{F}\) = O\(_2\)C\(_6\)F\(_4\)) was prepared according the literature. All air-sensitive compounds were stored in a glove box (Sylatech Y-05-G-7986) under N\(_2\) atmosphere. Purity and identity of the compounds were confirmed by high-resolution multinuclear NMR spectroscopy, elemental analysis and single crystal X-Ray diffraction. \(^{19}\)F- and \(^{29}\)Si-NMR spectra were collected with a Bruker Avance II 400 or Bruker Avance III 600 NMR spectrometer and referenced to the solvent in use. Chemical shifts are reported as dimensionless \(\delta\) values in ppm. Electrospray ionization mass spectra were obtained with a JEOL AccuTOF GCx Instrument. ATR-IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer and processed with MicroLab PC and Spectragryph v1.2.14.

2. Synthetic Procedures

2.1 Compound 1: [Si(cat\(^\text{F}\)\(_2\)]\(_2\)·solvent

Bis acetonitrile adduct Si(cat\(^\text{F}\)\(_2\)·(CH\(_3\)CN)\(_2\) (cat\(^\text{F}\) = O\(_2\)C\(_6\)F\(_4\)) was prepared according the literature. The solid compound was sublimed at 250 °C under 5.0·10\(^{-2}\) mbar dynamic vacuum for four hours. Under such conditions, the coordinated MeCN dissociated first, as was observed by IR-spectroscopy (see Ref\(^{1b}\) and Figure S1), followed by the sublimation of putative, monomeric Si(cat\(^\text{F}\)\(_2\)). At the given conditions, 38 wt% of Si(cat\(^\text{F}\)\(_2\)) sublime at the cooling finger. The remaining sublimation sump is insoluble in common aprotic non-donor solvents and does not show characteristic MeCN-vibrating or OH bands in the IR spectra. Upon hydrolysis of the sump, perfluorocatechol is formed, which indicates that it consists of long chain oligomers/polymers of the constitution [Si(cat\(^\text{F}\)\(_2\)]\(_n\). During the sublimation process, the partial formation of perfluorocatechol was observed in a variable amount. It is unclear where the required protons are originated from. The formation of cat\(^\text{F}\)OH is observed irrespective of the reaction solvents during the preparation of Si(cat\(^\text{F}\)\(_2\)), as well as in reactions conducted in silanized glassware or PTFE vessels. Nevertheless, the presence of cat\(^\text{F}\)OH does not influence the formation of the macrocycle.

Elemental analysis of the sublimate: calc. for [Si(cat\(^\text{F}\)\(_2\)]\(_2\): C 37.13, O 16.49, F 39.15, Si 7.23; found: C 37.26.

Mass Spectra (EI) of the sublimate: \(m/z\) calc. for C\(_{12}\)HF\(_4\)O\(_2\)Si\(^+\) = 388.95; found: 388.7.

For IR-spectroscopy, see section 3 in the supporting information.

The white powdery sublimate dissolved (>43 wt%) in various solvents (dichloromethane, chlorobenzene, fluorobenzene, o-difluorobenzene) and was separated from the remaining solids before crystallization. The amount of formed crystalline material was determined to be in a range of 40-50 wt%.
1(CH₂Cl₂)ₙ: Colorless crystals of 1 containing a total of 17 dichloromethane molecules (9 squeezed and 8 located outside the ring) per formula unit were obtained from a saturated solution of the sublimate in dichloromethane.

NMR-signals of the saturated solution prior to crystallization:

**¹⁹F-NMR** (376 MHz, CD₂Cl₂, 295 K): δ = −158.1, −158.5, −162.6, −163.0 ppm.

**¹³C-NMR** and **²⁹Si-NMR** spectra could not be obtained due to limited solubility in dichloromethane.

1(C₆H₅Cl)ₓ: Colorless crystals of 1 containing a total of 12 chlorobenzene molecules (all squeezed) per unit cell were obtained from a saturated solution of the sublimate in chlorobenzene.

NMR-signals of the saturated solution prior to crystallization:

**¹⁹F-NMR** (376 MHz, C₆H₅Cl, 295 K): δ = −158.1, −161.9 ppm.

**²⁹Si-NMR** spectra could not be obtained due to limited solubility in chlorobenzene.

1(C₆H₅F)₅: Colorless crystals of 1 containing a total of 16 fluorobenzene molecules (3 squeezed in a void inside the ring, 2 located on the rim-region and 11 located outside the ring) per formula unit were obtained from a saturated solution of the sublimate in fluorobenzene.

NMR-signals of the saturated solution prior to crystallization:

**¹⁹F-NMR** (376 MHz, C₆H₅F, 295 K): δ = −158.3, −162.3 ppm.

**²⁹Si-NMR** (119 MHz, C₆H₅F, 295 K): δ = −100.5, −100.8 ppm.

1(C₆H₄F₂)₃: Colorless crystals of 1 containing a total of 16 o-difluorobenzene molecules (6 squeezed in a void outside and 2 squeezed in a void inside the ring, 1 located on the rim-region and 7 located outside the ring) per unit cell were obtained from a saturated solution of the sublimate in o-difluorobenzene.

NMR-signals of the saturated solution prior to crystallization:

**¹⁹F-NMR** (376 MHz, o-C₆H₄F₂, 295 K): δ = −158.0, −162.6 ppm.

**²⁹Si-NMR** (119 MHz, o-C₆H₄F₂, 295 K): δ = −100.6, −101.0 ppm.

Attempts to characterize the macrocyclic compound or possible oligomers during the formation process by mass spectrometry were attempted with MALDI, EI, ESI, LIFDI, and DART. Unfortunately, no suitable signals of larger fragments could be observed, likely provoked by the high moisture sensitivity of the oligomers.

2.1 Compound 1₁(B₁₀C₂H₁₂)₂

Si(cat)₂·(CH₃CN)₂ was sublimed at 250 °C under 5.0·10⁻² mbar dynamic vacuum for four hours. The white powdery sublimate was dissolved in dichloromethane and separated from the remaining solids. A solution of o-carborane B₅H₁₂ in dichloromethane was added, and the mixture was crystallized via gaseous diffusion of pentane at room temperature. No evidence of host-guest interaction in solution could be obtained by **¹⁹F or **¹³B NMR spectroscopy.
3. Comparison of Si(cat)$^2$(MeCN)$_2$, Sublimate and Macrocycle

IR spectra at different stages of preparation were recorded. While the spectrum of the starting material Si(cat)$^2$(MeCN)$_2$ shows MeCN-vibrating bands ($\nu = 3001, 2936, 2336$ and $2311$ cm$^{-1}$, Figure S1a), they are absent in the spectra of the sublimate and the macrocycle. The spectra of the sublimate and the crystalline macrocyclic 1(C$_6$H$_4$F$_2$)$_4$ reveal shifted bands (cf. Figure S1b and c). This supports the presence of different constitutional states in the sublimate and the macrocycle.

Figure S1: ATR-IR spectra of a) Si(cat)$^2$(MeCN)$_2$; b) after sublimation and c) after crystallization from o-difluorobenzene.
4. Monitoring oligomerization by $^{19}$F-NMR in fluoro- and o-difluorobenzene

$^{19}$F-NMR spectra were taken at different times after dissolving the sublimate. In o-difluorobenzene and fluorobenzene, the rise of several new high-field shifted peaks is observed. This change is in line with a spontaneous oligomerization at room temperature. Signals of the tentative monomer Si(cat')$_2$ are at -157.8 and -162.4 ppm in o-difluorobenzene.

![Figure S2: $^{19}$F-NMR spectra of the sublimate in o-difluorobenzene (left) and fluorobenzene (right). After 2 h (blue), 10 h (red), 24 h (green), 48 h (purple), and after 2 weeks (yellow) in solution.](image)

![Figure S3: $^{29}$Si-NMR spectra of the sublimate in o-difluorobenzene after a) 9 h and after b) 48 h in solution.](image)
5. DOSY-NMR Measurements

$^1$H- and $^{19}$F-NMR based diffusion ordered spectroscopy (DOSY) experiments were performed in o-difluorobenzene at 295 K on a Bruker AVANCE II 400 NMR, using a stimulated echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (BPP-LED) with the standard Bruker pulse program, ledbpgpp2s. The gradient strength was linearly incremented in 16 steps from 2% up to 95% of the maximum gradient strength. Diffusion times and gradient pulse durations were optimized for each experiment in order to achieve a 95% decrease in the resonance intensity at the largest gradient amplitude. After Fourier transformation and phase correction, the diffusion dimension of the 2D DOSY spectra were processed by means of the Bruker Topspin software package (version 4.0.8) and analyzed with the Bruker Dynamics Center (version 2.6). Spectra of the sublimate 1 as well as monomeric Si(cat$^{tBu}$)$_2$ for comparison were measured, and the mean values are taken from the calculated diffusion coefficients (D) for each marked NMR peak.

Well in line with the computationally predicted formation of covalent oligomerization (vide infra), $^{19}$F DOSY-NMR on the solution phase samples of the sublimate revealed a range of diffusion constants ($D = 4.39 - 5.14E-10 \text{ m}^2 \text{ s}^{-1}$) indicating larger hydrodynamic radii as for those of distinct monomeric forms (for example Si(cat$^{tBu}$)$_2$ with $D = 8.79E-10 \text{ m}^2 \text{ s}^{-1}$). The fact that Si(cat$^{tBu}$)$_2$ is present as a monomer is confirmed by its $^{29}$Si-NMR shift of $\delta = -36.6$ ppm (MAS, 99 MHz), which agrees well with the computed shift ($-35.5$ ppm, see section 7 for computational details).

![Figure S4](image-url)

| signal | shift [ppm] | $D$ [m$^2$ s$^{-1}$] | error  | signal | shift [ppm] | $D$ [m$^2$ s$^{-1}$] | error  |
|--------|-------------|---------------------|--------|--------|-------------|---------------------|--------|
| 1      | -158.51     | 4.42E-10            | 1.09E-11| 1      | 1.36       | 8.74E-10           | 3.38E-12|
| 2      | -158.80     | 5.14E-10            | 5.35E-11| 2      | 1.34       | 8.85E-10           | 4.18E-12|
| 3      | -163.02     | 4.39E-10            | 1.12E-11| 3      | 1.24       | 8.81E-10           | 4.18E-12|
| 4      | -163.22     | 4.82E-10            | 3.12E-11| 4      | 1.24       | 8.81E-10           | 4.18E-12|
| 5      | -163.30     | 4.91E-10            | 2.87E-11| 5      | 1.24       | 8.81E-10           | 4.18E-12|
| avg.   | 4.74E-10    |                     |        | avg.   | 8.79E-10   |                     |        |
6. X-Ray Diffraction

Single Crystal-XRD

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Bruker D8 Venture diffractometer, dual-source (Mo or Cu-K\(\alpha\) radiation, microfocus X-ray tube, Photon III detector). Data were processed with the standard Bruker (SAINT, APEX3) software package. Multiscan absorption correction was applied using the SADABS program. The structures were solved by intrinsic phasing and refined using the SHELXTL software package (Version 2014/6 and 2018/3). Graphical handling of the structural data during solution and refinement was performed with OLEX2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model.

Electron density attributed to solvent of crystallization (dichloromethane, chlorobenzene, fluorobenzene or o-difluorobenzene) which could not be modeled was removed from the structures of 1(CH\(_2\)Cl)\(_6\), 1(C\(_6\)H\(_5\)Cl)\(_6\), 1(C\(_6\)H\(_7\)F)\(_6\) and 1(C\(_6\)H\(_8\)F\(_2\))\(_3\) with the BYPASS procedure, as implemented in PLATON (squeeze/hybrid). Partial structure factors from the solvent masks were included in the refinement as separate contributions to \(F_{\text{calc}}\).

For 1(CH\(_2\)Cl)\(_6\), 724 electrons were found in a volume of 2104 Å\(^3\) in one void per unit cell. This is consistent with the presence of 18 CH\(_2\)Cl per unit cell (9 per formula unit), which account for 756 electrons per unit cell. Since the detected void stretches beyond the cavity of the macrocycle, a definite number of hosted CH\(_2\)Cl molecules could not be determined, resulting in the composition 1(CH\(_2\)Cl)\(_6\). Additionally, 8 CH\(_2\)Cl molecules are located at the outside of the ring.

For 1(C\(_6\)H\(_5\)Cl)\(_6\), 2716 electrons were found in a volume of 9585 Å\(^3\) in one void per unit cell. This is consistent with the presence of 48 C\(_6\)H\(_5\)Cl per unit cell (12 per formula unit), which account for 2784 electrons per unit cell. Since the detected void stretches beyond the cavity of the macrocycle, a definite number of hosted C\(_6\)H\(_5\)Cl molecules could not be determined, resulting in the composition 1(C\(_6\)H\(_5\)Cl)\(_6\). For 1(C\(_6\)H\(_7\)F)\(_6\), 278 electrons were found in a volume of 948 Å\(^3\) in one void per unit cell. This is consistent with the presence of 6 C\(_6\)H\(_7\)F per unit cell (3 per formula unit), which account for 300 electrons per unit cell. Another two molecules of C\(_6\)H\(_7\)F are located at the rim-positions. This results in a total of 5 C\(_6\)H\(_7\)F molecules per formula unit (1(C\(_6\)H\(_7\)F)\(_5\)). Additionally, 11 C\(_6\)H\(_7\)F molecules are located at the outside of the ring.

For 1(C\(_6\)H\(_8\)F\(_2\))\(_3\), 732 and 234 electrons were found in a volume of 2464 and 682 Å\(^3\) in two voids per unit cell. This is consistent with the presence of 12 and 4 C\(_6\)H\(_8\)F\(_2\) per unit cell (6 and 2 per formula unit), which accounts for 696 and 232 electrons per unit cell. Since the second detected void is located in the cavity, and one C\(_6\)H\(_8\)F\(_2\) molecule is located at the rim-position, we suggest the composition 1(C\(_6\)H\(_8\)F\(_2\))\(_3\). Additionally, 7 C\(_6\)H\(_8\)F\(_2\) molecules are located at the outside of the ring.

For 1n(B\(_{10}\)C\(_{12}\)I\(_2\))\(_2\), no masking was performed. Although the obtained data is quite weak, the position of the \(\alpha\)-carborane was assured. As the X-ray scattering factors for boron and carbon are very similar, the absolute assignments should be regarded as tentative.

Data quality of 1(C\(_6\)H\(_5\)Cl)\(_6\) and 1(C\(_6\)H\(_8\)F\(_2\))\(_3\) was considered to be insufficient for deposition in CCDC and is solely given in the Supplementary Information. Crystallographic data for the other structures is deposited within the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2015065 (1(CH\(_2\)Cl)\(_6\)), 2015067 (1(C\(_6\)H\(_7\)F)\(_6\)) and 2015062 (1n(B\(_{10}\)C\(_{12}\)I\(_2\))\(_2\)) and can be obtained free of charge. Crystal data and structure are summarized in the tables under the crystallographic figure. The checkCif alerts B are commented in the respective CIF-files.
6.1 Compound 1(CH₂Cl₂)x (Squeezed solvent molecules not illustratable)
6.2 Compound 1(C₆H₅Cl)ₓ (Squeezed solvent molecules not illustratable)

| Identification code          | mo_dh317o_CIPh_0m_Cc    |
|-----------------------------|-------------------------|
| Empirical formula           | C₂₄₀Cl₁₂F₁₁₂H₆₀O₅₆Si₁₄  |
| Formula weight              | 6785.46                 |
| Temperature/K               | 100.0                   |
| Crystal system              | monoclinic              |
| Space group                 | C2/c                    |
| a/Å                         | 41.093(3)               |
| b/Å                         | 21.6967(17)             |
| c/Å                         | 31.155(3)               |
| α/°                         | 90                      |
| β/°                         | 111.442(3)              |
| γ/°                         | 90                      |
| Volume/Å³                   | 25855(4)                |
| Z                           | 4                       |
| ρcalc g/cm³                 | 1.396                   |
| μ/mm⁻¹                      | 0.214                   |
| F(000)                      | 10640.0                 |
| Crystal size/mm³            | 0.213 × 0.142 × 0.066   |
| Radiation                   | Mo Kα (λ = 0.71073)     |
| 2Θ range for data collection/° | 3.706 to 49.998          |
| Index ranges                | -46 ≤ h ≤ 47, -25 ≤ k ≤ 25, -37 ≤ l ≤ 37 |
| Reflections collected       | 126807                  |
| Independent reflections     | 21512 [Rint = 0.1812, Rsigma = 0.1374] |
| Data/restraints/parameters  | 21512/0/1577            |
| Goodness-of-fit on F²       | 1.051                   |
| Final R indexes [I>=2σ(I)]  | R₁ = 0.1107, wR₂ = 0.3084 |
| Final R indexes [all data]  | R₁ = 0.1950, wR₂ = 0.3695 |
| Largest diff. peak/hole/e Å³ | 0.69/-0.47             |
### 6.3 Compound \(1(C_6H_5F)_5\)

| Property                      | Value                  |
|-------------------------------|------------------------|
| Identification code           | mo_dh320_MZ_fph_0m     |
| Empirical formula             | \(C_{264}H_{80}F_{128}O_{56}S_{14}\) |
| Formula weight                | 6972.92                |
| Temperature/K                 | 100.0                  |
| Crystal system                | monoclinic             |
| Space group                   | \(P2_1/n\)             |
| \(a/\AA\)                     | 17.812(2)              |
| \(b/\AA\)                     | 20.220(2)              |
| \(c/\AA\)                     | 37.369(4)              |
| \(\alpha/°\)                  | 90                     |
| \(\beta/°\)                   | 91.190(4)              |
| \(\gamma/°\)                  | 90                     |
| Volume/\(\AA^3\)             | 13456(3)               |
| \(Z\)                         | 2                      |
| \(\rho_{\text{calc}}\) \(g/cm^3\) | 1.650                  |
| \(\mu/mm^{-1}\)              | 0.230                  |
| \(F(000)\)                    | 6620.0                 |
| Crystal size/\(mm^3\)         | 0.165 \times 0.111 \times 0.086 |
| Radiation                     | Mo \(K\alpha\) \((\lambda = 0.71073)\) |
| 2\(\theta\) range for data collection/° | 3.774 to 54.47 |
| Index ranges                  | -22 \(\leq h \leq 22, -25 \leq k \leq 25, -48 \leq l \leq 47\) |
| Reflections collected         | 287088                 |
| Independent reflections       | 29865 \([R_{\text{int}} = 0.0806, R_{\text{sigma}} = 0.0434]\) |
| Data/restraints/parameters    | 29865/584/2120         |
| Goodness-of-fit on \(F^2\)    | 1.051                  |
| Final R indexes [\(I>=2\sigma(I)\)] | \(R_1 = 0.1487, wR_2 = 0.3903\) |
| Final R indexes [all data]    | \(R_1 = 0.1665, wR_2 = 0.4003\) |
| Largest diff. peak/hole / \(e \AA^{-3}\) | 1.02/-0.89 |
6.4 Compound \( \text{I(C}_{6}\text{H}_{4}\text{F}_{2})_3 \)

| Identification code       | mo_dh320_odf_2_0m       |
|---------------------------|-------------------------|
| Empirical formula         | \( \text{C}_{26}\text{F}_{14}\text{H}_{32}\text{O}_{56}\text{Si}_{14} \) |
| Formula weight            | 7228.15                 |
| Temperature/K             | 100.0                   |
| Crystal system            | monoclinic              |
| Space group               | \( \text{Pn} \)         |
| \( a/\text{Å} \)          | 18.0278(11)             |
| \( b/\text{Å} \)          | 20.1432(12)             |
| \( c/\text{Å} \)          | 37.609(2)               |
| \( \alpha/\degree \)      | 90                      |
| \( \beta/\degree \)       | 89.986(2)               |
| \( \gamma/\degree \)      | 90                      |
| Volume/\( \text{Å}^3 \)   | 13657.2(14)             |
| \( Z \)                   | 2                       |
| \( \rho_{\text{calc}} \text{g/cm}^3 \) | 1.758            |
| \( \mu/\text{mm}^1 \)     | 0.244                   |
| \( F(000) \)              | 7112.0                  |
| Crystal size/\( \text{mm}^3 \) | 0.201 \times 0.194 \times 0.123 |
| Radiation                 | MoK\( \alpha \) (\( \lambda = 0.71073 \)) |
| \( 2\Theta \) range for data collection/\( \degree \) | 3.826 to 52.81 |
| Index ranges              | \(-22 \leq h \leq 22, -25 \leq k \leq 25, -47 \leq l \leq 46 \) |
| Reflections collected     | 299855                  |
| Independent reflections   | 53977 [\( R_{\text{int}} = 0.0579, R_{\text{sigma}} = 0.0430 \)] |
| Data/restraints/parameters| 53977/6838/3728         |
| Goodness-of-fit on \( F^2 \) | 2.267                  |
| Final R indexes [\( I \geq 2\sigma(I) \)] | \( R_1 = 0.1744, \text{wR}_2 = 0.4556 \) |
| Final R indexes [all data] | \( R_1 = 0.1865, \text{wR}_2 = 0.4739 \) |
| Largest diff. peak/hole / \( e \text{ Å}^3 \) | 1.47/-1.55             |
| Flack parameter           | 0.46(3)                 |
6.5 Compound $\text{1N}(\text{B}_{10}\text{C}_{2}\text{H}_{12})_2$

| Identification code       | mo\_dh\_SicatF2\_sub0301\_0m |
|---------------------------|--------------------------------|
| Empirical formula         | $\text{C}_{192}\text{H}_{108}\text{B}_{70}\text{F}_{112}\text{O}_{56}\text{Si}_{14}$ |
| Formula weight            | 6588.74                        |
| Temperature/K             | 100.0                          |
| Crystal system            | monoclinic                     |
| Space group               | $\text{P2}_1/n$                |
| $a$/Å                     | 20.4453(14)                    |
| $b$/Å                     | 18.4175(14)                    |
| $c$/Å                     | 36.352(3)                      |
| $\alpha$/°                | 90                             |
| $\beta$/°                 | 94.061(2)                      |
| $\gamma$/°               | 90                             |
| Volume/Å³                 | 13654.0(17)                    |
| $Z$                       | 2                              |
| $\rho_{\text{calc}}$/cm³ | 1.603                          |
| $\mu$/mm³                 | 0.215                          |
| $F(000)$                  | 6524.0                         |
| Crystal size/mm³          | $0.118 \times 0.117 \times 0.051$ |
| Radiation                 | Mo $K_\alpha$ ($\lambda = 0.71073$) |
| $2\Theta$ range for data collection/° | 3.994 to 51.998 |
| Index ranges              | $-25 \leq h \leq 25, -22 \leq k \leq 17, -44 \leq l \leq 44$ |
| Reflections collected     | 136560                         |
| Independent reflections   | 26405 [$R_{\text{int}} = 0.1465, R_{\text{sigma}} = 0.1159$] |
| Data/restraints/parameters | 26405/1955/2103                |
| Goodness-of-fit on $F^2$  | 1.018                          |
| Final $R$ indexes [$I \geq 2\sigma (I)$] | $R_1 = 0.0982$, $wR_2 = 0.2675$ |
| Final $R$ indexes [all data] | $R_1 = 0.2066$, $wR_2 = 0.3453$ |
| Largest diff. peak/hole / e Å³ | 0.67/-0.56                   |
Powder-XRD

Powder X-Ray diffraction data were recorded with a STOE STADI P diffractometer (Cu-Kα radiation, λ = 1.5406 Å, Ge(111)-monochromated) in sealed glass capillaries as sample containers (Ø = 0.5 mm) in transmission mode.

Attempts to characterize the sublimate before crystallization were made by X-ray powder diffraction. The starting material Si(cat^F)_2·(CH_3CN)_2 as well as the sublimated compound, are amorphous solids. By contrast, after recrystallization (from dichloromethane) the macrocycle is crystalline with sharp diffraction peaks in the XRD pattern (2θ = 5.1 (100), 3.6 (56), 7.9 (46) and 9.4 (45)).

Figure S5: X-ray powder diffraction patterns of a) Si(cat^F)_2·(CH_3CN)_2; b) the sublimate and c) macrocycle 1(CH_2Cl)_2 after recrystallization (red: computed X-ray powder diffraction pattern).
7. Computational Section

Assessment of the dimerization and trimerization of Si(cat′)₂ units and the dissociation of CH₃CN.

Energetics and ²⁹Si-NMR shifts.

Geometry optimizations and single point energy calculations have been performed with ORCA 4.2.¹⁰ The structures of all involved compounds were optimized with the PBEh-3c/def2-mSVP as implemented in ORCA, using grid5 settings.¹¹ All calculated structures have been confirmed as energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level, revealing only positive Hessian eigenvalues, or one negative in case of the transition state. Enthalpies at 298.15 K have been calculated at the same level of theory by using the rigid-rotor harmonic oscillator (RRHO) approximation,¹² as implemented in ORCA.

Final single point energies for the structures were obtained with double-hybrid DSD-BLYP¹³, including Grimme’s semi-empirical dispersion correction¹⁴ with Becke-Johnson damping function¹⁵ (D3(BJ) and the def2-QZVPP¹⁶ basis set. In all DFT computations, the resolution-of-identity¹⁷ and “chain of spheres”¹⁸ approximation in the form of RIJCOSX was used in combination with matching auxiliary basis sets (def2/J).¹⁹ For the double-hybrid functionals, including MP2 correlation, the def2/C auxiliary basis set was applied.

Solvation free energies were obtained by COSMO-RS in dichloromethane as implemented in ADF²⁰ based on BP86/TZP²¹ single point energy calculations for the electrostatic solute-solvent interaction on the PBEh-3c gas-phase structures.²²

²⁹Si-NMR chemical shifts were calculated based on the PBEh-3c gas-phase structures using the respective modules²³ in the ADF program package, with the PBE0 hybrid functional²⁴ and a triple-ζ Slater type basis set (TZ2P)²⁵, in which relativistic spin-orbit contributions to the magnetic shielding constants were treated by the two-component zero-order regular approximation (SO-ZORA).²⁶ NMR chemical shifts are given relative to TMS (0 ppm), calculated at the same level of theory.

The numerical data and a summary of all the relevant values can be found in table S1.

For the adduct of formation of Si(cat′)₂ with fluorobenzene, a stable trans-adduct was obtained if the structure optimization was performed in a dielectric continuum model (CPCM/CH₂Cl₂), yielding very unfavorable energetics (ΔH = -0.7 kJ mol⁻¹ and ΔG = 113.9 kJ mol⁻¹). With o-difluorobenzene, no stable adduct could be identified at the solvation corrected potential energy surface.
Table S1: Numerical data and summary of all relevant values for the dimerization and trimerization of Si(cat\(^F\)\)\(_2\) units and the dissociation of CH\(_3\)CN.

| Compound | \(E\) [Hartree] | Enth. Corr. | \(T^\circ\)S | \(E\) [Hartree] | \(H\) [kJ mol\(^{-1}\)] | \(G\) [kJ mol\(^{-1}\)] | \(G(COSMO-RS)\) [kJ mol\(^{-1}\)] | comp. \(^29^\text{Si}-\text{NMR}\) |
|----------|-----------------|-------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Si(cat\(^F\)\)\(_2\) | -1842.9984 | 365.3 | 174.6 | -1845.6675 | -4845.800.0 | -4845.434.6 | -4845.609.2 | -4845.648.2 | -34.68 |
| "Precomplex" | -3686.0192 | 735.0 | 283.8 | -3691.3571 | -9691.658.1 | -9690.923.1 | -9691.206.8 | -9691.267.7 | -34.88 |
| [Si(cat\(^F\)\)\(_2\)]\(_2\) | -3686.0304 | 735.3 | 285.6 | -3691.3695 | -9691.690.6 | -9690.955.3 | -9691.240.9 | -9691.312.5 | -65.96 |
| [Si(cat\(^F\)\)\(_2\)]\(_3\) | -5529.0570 | 1105.0 | 393.7 | -5537.0683 | -14537.572.8 | -14536.467.7 | -14536.861.4 | -14536.957.3 | -66.2 (avg) |

| transition state 1 | -3685.9926 | 732.7 | 275.7 | -3691.3285 | -9691.583.1 | -9690.850.4 | -9691.126.1 | -9691.197.8 | -114.7 |
| CH\(_3\)CN | -132.4540 | 134.6 | 74.7 | -132.6612 | -3483.021.1 | -3482.167.5 | -3482.243.2 | -3482.634.3 | -92.6 |
| trans-Si(cat\(^F\)\)\(_2\)(CH\(_3\)CN) | -2107.9498 | 641.0 | 215.8 | -2111.0214 | -5542.486.6 | -5541.845.6 | -5542.061.4 | -5542.170.4 | -136.9 |

| \(2\text{ Si(cat}\(^F\)\)\(_2\) \rightarrow \text{"Precomplex"}\) | 4.3 | -65.4 | -58.1 | -53.8 | 11.6 | 28.8 |
| \(2\text{ Si(cat}\(^F\)\)\(_2\) \rightarrow [\text{Si(cat}\(^F\)\)\(_2\)]\(_2\)\) | 4.6 | -63.6 | -90.6 | -86.0 | -22.5 | -16.1 |
| \(2\text{ Si(cat}\(^F\)\)\(_2\) \rightarrow TS1\) | 2.0 | -73.4 | 16.9 | 18.9 | 92.3 | 98.6 |
| \([\text{Si(cat}\(^F\)\)\(_2\)]\(_2\) + \text{Si(cat}\(^F\)\)\(_2\) \rightarrow [\text{Si(cat}\(^F\)\)\(_2\)]\(_3\)\) | 4.4 | -66.4 | -82.2 | -77.8 | -11.4 | 3.4 |
| \(\text{Si(cat}\(^F\)\)\(_2\) + 2\text{ CH}_3\text{CN} \rightarrow \text{trans-Si(cat}\(^F\)\)\(_2\)(CH}_3\text{CN)\)} | 6.4 | -108.1 | -82.4 | -76.0 | 32.1 | 4.6 |
| \(\text{Si(cat}\(^F\)\)\(_2\) + \text{CH}_3\text{CN} \rightarrow \text{Si(cat}\(^F\)\)\(_2\)(CH}_3\text{CN}\) | 3.5 | -53.4 | -18.0 | -14.5 | 38.9 | 11.7 |
| \(\text{Si(cat}\(^F\)\)\(_2\)(CH}_3\text{CN} + \text{CH}_3\text{CN} \rightarrow \text{trans-Si(cat}\(^F\)\)\(_2\)(CH}_3\text{CN)\)} | 2.9 | -54.7 | -64.4 | -61.6 | -6.9 | -7.1 |

Figure S6: Molecular structures (energetic minima calc. at PBEh-3c/def2-mSVP level of theory) of the dimerization and trimerization of Si(cat\(^F\)\)\(_2\) units and the dissociation of CH\(_3\)CN.
Assessment of the relative stability of acyclic and cyclic covalent oligomers $n = 2 – 20$ for $[\text{Si(cat}^4\text{)}_2]_n$

Generally, there are three different constitutional modes for bis(catecholato)silanes to oligomerize. In mode A, the silicon centers are bridged via one catecholate and have another catecholate attached in a bidentate fashion (Figure S1XX left). In mode B, either a cyclic (B), or an acyclic form (B') can be adopted. Herein, the silicon centers are bridged via two catecholate units, and in the acyclic form, the ends are capped by a bidentate catecholate.

Figure S7: schematic drawing of feasible bridging modes of $[\text{Si(cat}^4\text{)}_2]_n$, illustrated at the example of $[\text{Si(cat}^4\text{)}_2]_4$.

For $n = 2 – 11$ all three forms of possible covalent isomers were optimized by Grimme’s GFN1-xTB method, stationary points verified by the absence of imaginary frequencies and the thermal correction taken over for the next steps. Figure S8a shows the relative reaction enthalpy ($\Delta H_{\text{rel}}$) of every $n$-meric oligomer, which is calculated by division of the reaction enthalpy of every $n$-mer through the number of monomeric Si(cat$^4$)$_2$ moieties ($n$).

$$
\Delta H_{\text{rel}} = \frac{\Delta H}{n} = \frac{H(\text{n-mer}) - n\cdot H(\text{Si(cat}^4\text{)})}{n}
$$

eq. 1

Figure S8: a) reaction enthalpies of the different isomers of type A, B and B' (calc. by Grimme’s GFN1-xTB method) for $n = 1 – 11$ and b) relative reaction enthalpies of the isomer B' (calc. at PW6B95-D3/def2-TZVPP//HF-3c level of theory) for $n = 1 – 20$.

For $n > 6$, the macrocyclic structure of type B' becomes the most stable constitutional isomer. Those isomers of type B' were reoptimized at the HF-3c method,28 as implemented in ORCA 4.2. Final single point enthalpies were obtained on PW6B95-D3(BJ)/def2-TZVPP including Grimme’s semi-empirical dispersion correction with Becke-Johnson damping function, and the GFN1-xTB thermal/ZPE correction.15 The normalized reaction enthalpies of $\Delta H_{\text{rel}}$ were obtained in the same way as described above, eq. 1 (Figure S8b). A slump at $n = 14$ corresponds to the experimentally observed composition $\text{Si}_{14}(\text{O}_2\text{C}_6\text{F}_4)_{28}$.
Table S2: Numerical data and summary of all relevant values for the acyclic and cyclic oligomers of \([\text{Si(cat}^3]_n\) for \(n = 1 – 11\) calc. by Grimme’s GFN1-xTB method.

| Structure                  | Compound | \(E [\text{Hartree}]\) | \(E [\text{kJ mol}^{-1}]\) | \(H [\text{kJ mol}^{-1}]\) | \(G [\text{kJ mol}^{-1}]\) | \(\Delta E [\text{kJ mol}^{-1}]\) |
|----------------------------|----------|-------------------------|-----------------------------|-----------------------------|------------------------------|----------------------------------|
| **01mer**                  |          |                         |                             |                             |                              |                                  |
|                            |          | -87.301543              | -229210.17                  | -228870.31                  | -229060.50                   | 0.00                             |
| **02mer**                  |          |                         |                             |                             |                              |                                  |
|                            |          | -174.70994            | -458700.89                  | -916344.89                  | -458120.94                   | -140.27                          |
|                            |          | -262.08726            | -688110.03                  | -697089.61                  | -687510.13                   | -159.84                          |
|                            |          | -349.45711            | -917499.52                  | -916140.75                  | -916667.79                   | -164.71                          |
|                            |          | -436.80858            | -1146840.77                 | -1145141.49                 | -1145778.98                  | -157.98                          |
|                            |          | -524.19963            | -1376285.96                 | -1374243.04                 | -1375003.25                  | -170.82                          |
|                            |          | -611.55165            | -1605628.65                 | -1603250.17                 | -1604104.95                  | -165.35                          |
|                            |          | -698.95228            | -1835098.96                 | -1832371.54                 | -1833359.26                  | -177.20                          |
|                            |          | -786.33159            | -2064513.14                 | -2061444.88                 | -2062546.92                  | -180.18                          |
|                            |          | -873.62876            | -2293853.83                 | -2290456.35                 | -2291641.20                  | -175.21                          |
|                            |          | -961.09172            | -2523345.96                 | -2519593.24                 | -2520925.12                  | -184.92                          |
| **03mer**                  |          |                         |                             |                             |                              |                                  |
|                            |          | -174.70993            | -458700.89                  | -916344.89                  | -458120.94                   | -140.27                          |
|                            |          | -262.12893            | -688219.43                  | -687200.64                  | -687611.78                   | -196.31                          |
|                            |          | -349.54274            | -917724.35                  | -916363.94                  | -916866.35                   | -220.92                          |
|                            |          | -436.96152            | -1147424.31                 | -1145546.82                 | -1146164.23                  | -238.29                          |
|                            |          | -524.37517            | -1376746.83                 | -1374714.10                 | -1375432.83                  | -247.64                          |
|                            |          | -611.79474            | -1606266.88                 | -1603894.48                 | -1604719.09                  | -256.53                          |
|                            |          | -699.21583            | -1835790.92                 | -1833076.58                 | -1834013.09                  | -263.69                          |
|                            |          | -786.62885            | -2065293.76                 | -2062242.50                 | -2063277.69                  | -266.91                          |
|                            |          | -874.05243            | -2294824.34                 | -2291428.57                 | -2292581.67                  | -272.26                          |
|                            |          | -961.45768            | -2524306.75                 | -2520576.34                 | -2521826.92                  | -272.26                          |
| **04mer**                  |          |                         |                             |                             |                              |                                  |
|                            |          | -174.65144            | -458547.30                  | -457872.78                  | -458167.22                   | -63.48                           |
|                            |          | -262.08634            | -688107.60                  | -687086.12                  | -687504.23                   | -159.03                          |
|                            |          | -349.54682            | -917735.06                  | -916365.85                  | -916911.31                   | -223.60                          |
|                            |          | -436.97345            | -1147273.66                 | -1145567.57                 | -1146210.19                  | -244.56                          |
|                            |          | -524.43416            | -1376901.71                 | -1374858.47                 | -1375593.84                  | -273.45                          |
|                            |          | -611.87108            | -1606467.29                 | -1604077.23                 | -1604935.24                  | -285.16                          |
|                            |          | -699.29735            | -1836004.95                 | -1833274.98                 | -1834246.84                  | -290.45                          |
|                            |          | -786.73006            | -2065559.47                 | -2062482.58                 | -2063577.65                  | -296.44                          |
|                            |          | -874.15694            | -2295098.74                 | -2291689.21                 | -2292875.17                  | -299.70                          |
|                            |          | -961.56588            | -2524590.87                 | -2520839.64                 | -2522133.55                  | -298.09                          |
Figure S9: Selected structures (energetic minima calc. by Grimme’s GFN1-xTB method) of different covalent oligomers of [Si(catF)_2]_n; left: mode A, middle: mode B, right: mode B'; From top to bottom: n = 2, 4, 3, 6, 11.
Table S3: Numerical data and summary of all relevant values of oligomers B’ of [Si(cat)]$_n$ for $n = 1$ – 20, reoptimized with HF-3c, SP energies at PW6895-D3(BJ)/def2-TZVP level of theory; thermal corrections obtained from GFN1-xTB.

| Compound | $E$ [kJ mol$^{-1}$] | Enth. Corr. [kJ mol$^{-1}$] | $T^*$ [kJ mol$^{-1}$] | $E$ [Hartree] PW6895 | $E$ [kJ mol$^{-1}$] | $H$ [kJ mol$^{-1}$] | $G$ [kJ mol$^{-1}$] | $\Delta H/n$ [kJ mol$^{-1}$] | $\Delta G/n$ [kJ mol$^{-1}$] |
|----------|---------------------|--------------------------|------------------|------------------|------------------|----------------|----------------|----------------|----------------|
| 01mer    | -229210.17          | 339.85                   | 190.20           | -1849.19533      | -4855061.66      | -4854721.82    | -9709598.59    | 69.74           | 112.72         |
| 02mer    | -458547.30          | 674.51                   | 294.43           | -3698.33556      | -9709978.67      | -9709304.16    | -9709598.59    | 69.74           | 112.72         |
| 03mer    | -688107.60          | 1021.48                  | 418.11           | -5547.59824      | -14565217.17     | -14564195.70   | -14564613.81   | -10.08          | 40.75          |
| 04mer    | -917735.06          | 1369.21                  | 545.45           | -7396.84500      | -19420413.87     | -19419044.66   | -19419590.12   | -39.35          | 14.49          |
| 05mer    | -1147273.66         | 1706.08                  | 642.62           | -9246.11727      | -24275677.56     | -24273971.48   | -24274614.10   | -72.48          | -10.80         |
| 06mer    | -1376901.71         | 2043.24                  | 735.38           | -11095.35924     | -29130861.69     | -29128818.45   | -29129553.82   | -81.26          | -13.62         |
| 07mer    | -1606467.29         | 2390.06                  | 858.01           | -12944.57611     | -33985979.91     | -33983589.84   | -33984447.85   | -76.73          | -9.10          |
| 08mer    | -1836004.95         | 2729.97                  | 971.86           | -14793.80286     | -38841122.07     | -38838394.10   | -38839365.96   | -77.44          | -8.73          |
| 09mer    | -2065559.47         | 3076.89                  | 1095.07          | -16643.02426     | -43696254.19     | -43693177.31   | -43694272.37   | -75.66          | -7.13          |
| 10mer    | -2295098.74         | 3409.53                  | 1185.96          | -18492.24769     | -48551389.65     | -48547980.12   | -48549166.08   | -76.19          | -4.59          |
| 11mer    | -2524590.87         | 3751.23                  | 1293.91          | -20341.47309     | -53406530.27     | -53402797.04   | -53404072.95   | -76.28          | -3.70          |
| 12mer    | -2754133.02         | 4093.25                  | 1406.52          | -22190.67178     | -58261600.77     | -58257507.52   | -58258914.04   | -70.48          | 2.52           |
| 13mer    | -2983660.33         | 4437.90                  | 1521.97          | -24039.89523     | -63116736.26     | -63112298.36   | -63113820.33   | -70.36          | 2.76           |
| 14mer    | -3213185.39         | 4777.69                  | 1628.00          | -25889.17573     | -67972021.56     | -67967243.87   | -67968871.87   | -81.32          | -7.40          |
| 15mer    | -3442545.78         | 5122.90                  | 1739.70          | -27738.30851     | -72826919.00     | -72821796.10   | -72823535.80   | -64.59          | 9.63           |
| 16mer    | -3672196.00         | 5468.83                  | 1850.34          | -29587.52234     | -77682029.23     | -77676560.39   | -77678410.73   | -63.21          | 11.35          |
| 17mer    | -3901592.84         | 5799.90                  | 1944.97          | -31436.75229     | -82537181.81     | -82533181.91   | -82533266.88   | -65.35          | 10.44          |
| 18mer    | -4131306.38         | 6155.36                  | 2078.24          | -33285.96620     | -87392371.02     | -87386215.66   | -87388293.90   | -67.94          | 6.80           |
| 19mer    | -4360730.62         | 6494.62                  | 2188.78          | -35135.17171     | -92247380.67     | -92240886.05   | -92243074.83   | -61.66          | 13.34          |
| 20mer    | -4590183.82         | 6823.61                  | 2272.30          | -36984.43226     | -97102613.56     | -97095789.95   | -97098062.25   | -67.68          | 8.91           |
Figure S10: Overview of all optimized structures (HF-3c level of theory) of different oligomers B’ of [Si(catF)2]_n (n = 1 – 20).
8. NMR Spectra

$^{19}$F-NMR (376 MHz, CD$_2$Cl$_2$, 295 K) of the saturated CH$_2$Cl$_2$ solution prior to crystallization.

$^{19}$F-NMR (376 MHz, C$_6$H$_5$Cl, 295 K) of the saturated chlorobenzene solution prior to crystallization.

$^{19}$F-NMR (376 MHz, C$_6$H$_5$F, 295 K) of the saturated fluorobenzene solution prior to crystallization.
$^{29}$Si-NMR (119 MHz, C$_6$H$_5$F, 295 K) of the saturated fluorobenzene solution prior to crystallization.

$^{19}$F-NMR (376 MHz, o-C$_6$H$_4$F$_2$, 295 K) of the saturated o-difluorobenzene solution prior to crystallization.

$^{29}$Si-NMR (119 MHz, o-C$_6$H$_4$F$_2$, 295 K) of the saturated o-difluorobenzene solution prior to crystallization.
9. Literature

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