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## Fluorinated and Trifluoromethylated Corannulenes

Bernd M. Schmidt,<sup>[a, c]</sup> Berit Topolinski,<sup>[a, c]</sup> Mihoko Yamada,<sup>[a, b]</sup>  
Shuhei Higashibayashi,<sup>[c]</sup> Mitsuhiko Shionoya,<sup>[b]</sup> Hidehiro Sakurai,<sup>[c]</sup> and Dieter Lentz\*<sup>[a]</sup>

**Abstract:** The syntheses and properties of corannulenes carrying electron-withdrawing groups (F, CF<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>) are reported. Direct fluorination of corannulene (C<sub>20</sub>H<sub>10</sub>) was carried out with xenon difluoride, and the crystal structure of the product was confirmed by the X-ray analysis. Novel trifluoromethylated corannulenes, including the versatile 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene, were obtained by various established ring-closing reac-

tions. Besides the use of hexafluorobutylene for the construction of fluoranthenes by Diels–Alder reaction as precursor molecules to form 1,2-disubstituted corannulenes, bis(pentafluorophenyl)acetylene was employed as dienophile. The molecular structure

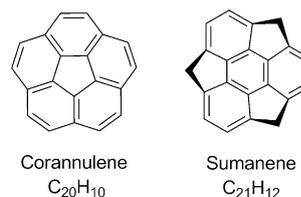
and crystal packing of a trifluoromethylated corannulene was determined by single-crystal X-ray analysis and compared with those known brominated and trifluoromethylated corannulenes. The general electron-acceptor properties of corannulenes bearing substituents introduced in particular positions by liquid-phase synthesis are discussed together with published computational results.

**Keywords:** corannulenes • electrochemistry • fluorine • stacking interactions • trifluoromethylation

### Introduction

Geodesic polyarenes, also called buckybowls, became the focus of attention not only because they can be considered as substructures of fullerenes with three-dimensional bowl shape or as the polar end caps of carbon nanotubes, but also because of their own chemical and physical properties. Corannulene (C<sub>20</sub>H<sub>10</sub>) and sumanene (C<sub>21</sub>H<sub>12</sub>) are the best-studied buckybowl compounds (Scheme 1). Corannulene has been known for more than four decades,<sup>[1]</sup> whereas sumanene was first synthesized in 2003 by Sakurai and co-workers.<sup>[2]</sup>

The chemistry of corannulenes is manifold and includes modification of the peripheral substituents leading to complex stereochemical, optical and electrochemical properties.<sup>[3]</sup> Other derivatives include bioconjugates,<sup>[4]</sup> push–pull systems,<sup>[5]</sup> supramolecular oligomers<sup>[6]</sup> and even curved radicals,<sup>[7]</sup> depending on the attached substituents. Rich organo-



Scheme 1. The buckybowls corannulene and sumanene.

metallic coordination chemistry was revealed.<sup>[8]</sup> The η<sup>6</sup> coordination of the curved carbon surface of corannulene, which was achieved in ruthenium<sup>[9]</sup> and osmium<sup>[9d]</sup> complexes, is accompanied by flattening of the corannulene bowl, so that two ruthenium complex ions can be coordinated.<sup>[9c]</sup> Other metal complexes include those with η<sup>2</sup> coordination (generating 1D infinite chains)<sup>[10]</sup> and mono-,<sup>[11]</sup> di-,<sup>[11,12]</sup> tetra-,<sup>[12]</sup> and penta-<sup>[12]</sup> σ-bonded complexes. These were obtained from the corresponding halogenated precursors by insertion. Cyclopalladated corannulenes were synthesized and their expanded π systems and columnar self-assembly in the solid state investigated.<sup>[13a]</sup>

Corannulene was also shown to be a precursor to further π-extended polycyclic aromatic hydrocarbons, such as the family of indenocorannulenes.<sup>[14]</sup> Starting from the symmetrical pentachlorocorannulene,<sup>[15]</sup> a short [5,5] single-walled carbon nanotube (C<sub>50</sub>H<sub>10</sub>) was synthesized by stepwise chemical methods with a final flash vacuum pyrolysis step.<sup>[16]</sup>

In contrast, despite some earlier attempts<sup>[17]</sup> and theoretical studies,<sup>[18]</sup> research on sumanene only began with its first successful synthesis in 2003.<sup>[2a]</sup> Subsequently its solid-state packing,<sup>[19]</sup> the formation of benzylic anions,<sup>[19a]</sup> bowl-to-

[a] Dr. B. M. Schmidt, B. Topolinski, Dr. M. Yamada, Prof. Dr. D. Lentz  
Freie Universität Berlin  
Institut für Chemie und Biochemie  
Fabeckstrasse 34-36, 14195 Berlin (Germany)  
E-mail: dieter.lentz@fu-berlin.de

[b] Dr. M. Yamada, Prof. Dr. M. Shionoya  
Department of Chemistry, Graduate School of Science  
The University of Tokyo, 7-3-1 Hongo  
Bunkyo-ku, Tokyo 113-0033 (Japan)

[c] Dr. B. M. Schmidt, B. Topolinski, Dr. S. Higashibayashi,  
Prof. Dr. H. Sakurai  
Institute for Molecular Science  
Myodaiji, Okazaki 444-8787 (Japan)

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bowl inversion behaviour<sup>[20c]</sup> and the selective synthesis of  $C_3$ -symmetric functionalized sumanenes<sup>[21]</sup> were pursued.

Hybrid forms of corannulene and sumanene were prepared recently by palladium-catalyzed cyclization reactions, creating bowls with increased curvature and unusual S-shaped transition state (in contrast to the planar transition states of corannulene and sumanene) with a very high inversion barrier.<sup>[22]</sup>

The chemistry and properties of electron-poor buckybowls were only scarcely investigated previously for fluorinated compounds.<sup>[23]</sup> This is surprising, because fluorination is one of the most effective methods to alter the properties of a chemical compound and is widely applied in the design of organic electronics and further applications.<sup>[24]</sup>

Heterogeneous gas-phase trifluoromethylation of corannulene with an excess of trifluoromethyl iodide was reported in 2012. The crude product was purified by extensive HPLC, and only one product, namely, pentakis(trifluoromethyl)corannulene, could be separated from the complex mixture, in 15% yield.<sup>[25]</sup>

In continuation of our work,<sup>[26]</sup> we present our detailed study on the synthesis and properties of corannulenes bearing electron-withdrawing groups, solely prepared by liquid-phase synthesis (Scheme 2).

## Results and Discussion

In principal, three options can be considered for introducing fluorine into buckybowls: 1) substitution of an aromatic hydrogen atom at the rim of the bowl with a fluorine atom; 2) introduction of side chains or rings bearing electron-withdrawing fluorine atoms; 3) in sumanene, the benzylic  $CH_2$

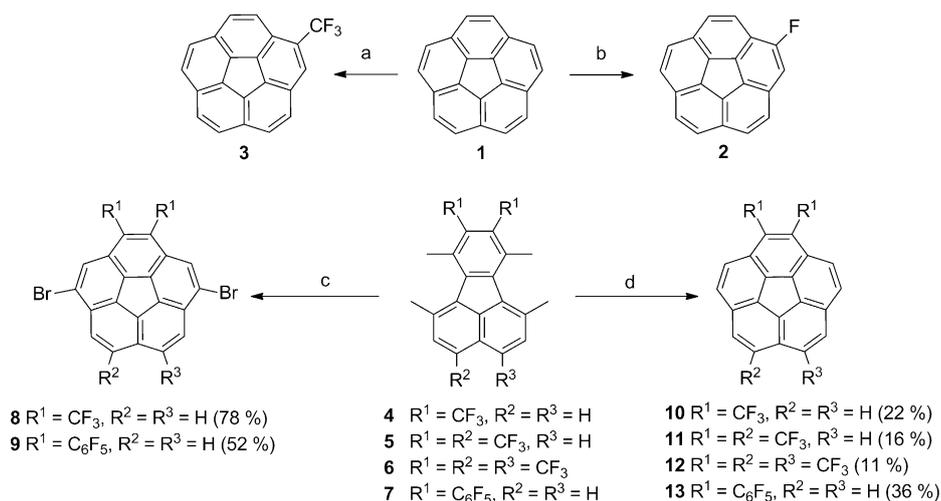
groups are also suitable for introduction of fluorine. We recently reported the synthesis of hexafluorosumanene and its congeners;<sup>[26a]</sup> therefore, its discussion is omitted here.

**Syntheses:** Despite the success of halogen exchange (halex) reactions in industry at high reaction temperatures and Pd-mediated formation of aryl fluorides, the synthesis of fluorinated aromatics is still challenging. For instance, reactions involving an aryne intermediate lead to the formation of regioisomers, and the corresponding hydrogen compounds (proto-dehalogenated) are commonly observed by-products in many cases.<sup>[27]</sup> We opted to use the commercially available xenon difluoride, because it allows direct introduction of a fluorine substituent even in unactivated aromatic compounds.<sup>[28]</sup>

Xenon difluoride was added to corannulene (**1**) at low temperature in dichloromethane and the reaction mixture slowly warmed to room temperature, at which the reaction occurs after some latency time. The crude reaction product consisted of a mixture of unconsumed corannulene, the desired monofluorocorannulene and traces of di- and trisubstituted compounds. Monofluorocorannulene (**2**) was separated from the crude reaction product by reverse-phase HPLC, because it could not be separated from **1** by column chromatography or recycling HPLC. Because of the overall simplicity of the fluorination reaction (despite the purification issues), we made several attempts to obtain higher fluorinated corannulenes. <sup>19</sup>F NMR spectroscopy revealed that difluorinated corannulenes were also obtained, as indicated by a series of doublets between  $-116$  and  $-119$  ppm exhibiting  $^3J(F,H)$  coupling constants of approximately 13 Hz. However, efforts to separate the difluorinated corannulenes by silica-gel column chromatography and normal-phase HPLC (Buckyprep column) failed.

Subsequent fluorination reactions of **2** or those starting from **1** suffered from severely decreased amounts of recovered material, most likely due to polymerization of the compounds. The substitution of up to three hydrogen atoms by fluorine could be observed by mass spectrometry, but isolation was not possible. Fluorination is assumed to have a weaker effect on the electron-acceptor properties than trifluoromethylation and even chlorination,<sup>[25]</sup> as is discussed below.

Recently, we reported on the syntheses and properties of trifluoromethylated corannulenes from corannulene,<sup>[26c]</sup> and obtained monotrifluoromethylcorannulene (**3**) by a direct reaction using Togni's reagent (1-

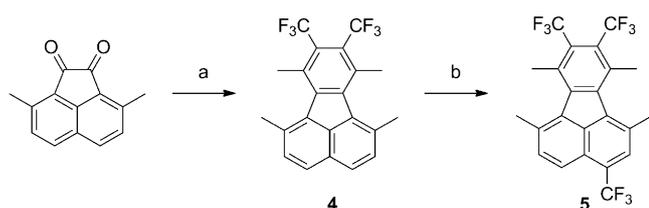


Scheme 2. Syntheses of corannulenes bearing electron-withdrawing groups by liquid-phase syntheses. a) 1-Trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (Togni's acid reagent; 1.0 equiv), methyltrioxorhenium (0.1 equiv), 1,2-dichloroethane, 80 °C, 8 h, 19%; b) xenon difluoride (1.4 equiv),  $CH_2Cl_2$ ,  $-78$  °C to RT, 3 h, 34%; c) *N*-bromosuccinimide (12.0 equiv), AIBN or DBPO (0.03 equiv), 24 h, 80 °C, then sodium hydroxide (10.0 equiv), dioxane/water (12:5), 110 °C, 20 min; d) *N*-bromosuccinimide (12.0 equiv), AIBN or DBPO (0.03 equiv), 24 h, 80 °C, then nickel powder (8.8 equiv), DMF, 80 °C, 8 h.

trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one, now also called Togni Reagent I) in the presence of methyltrioxorhenium;<sup>[29]</sup> although the yield is rather poor, monosubstituted derivative **3** can be purified simply by column chromatography.

To avoid the formation of positional isomers when converting a monofunctionalized corannulene to a disubstituted compound, it is feasible to introduce the desired substituent in an earlier stage of the synthesis. It seemed reasonable to introduce two trifluoromethyl groups into a precursor molecule of the corresponding corannulene for successive construction of the target molecule. Corannulene is prepared usually by a ring-closing reaction after obtaining a corresponding fluoranthene. Scott et al.,<sup>[30]</sup> Siegel et al.<sup>[31]</sup> and Rabideau, Sygula et al.<sup>[32]</sup> used norbornadiene as dienophile for the construction of the tetramethylfluoranthene after subsequent CO loss and Retro-Diels–Alder reaction. Siegel and co-workers showed that dimethyl acetylenedicarboxylate can be used to synthesize the respective fluoranthene with two methylcarboxylate groups in *ortho* positions,<sup>[33a]</sup> and this method was later taken up again.<sup>[33b]</sup> We therefore reasoned that hexafluorobutyne should also be applicable, since it is a particularly electrophilic acetylene and hence a potent dienophile, and may circumvent the formation of regioisomers by a regioselective reaction. After work-up by column chromatography, the desired 1,6,7,10-tetramethyl-8,9-bis(trifluoromethyl)fluoranthene (**4**) could be isolated in 76% yield and converted to the desired 1,2-bis(trifluoromethyl)corannulene (**10**) in 22% yield.<sup>[26c]</sup>

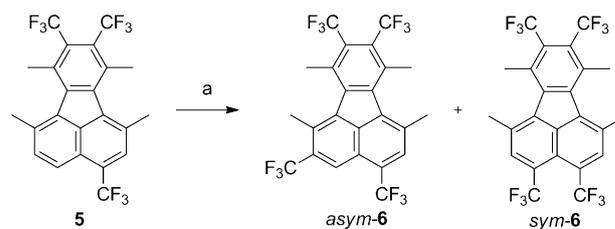
The synthesis of a tris(trifluoromethylated)corannulene was pursued as follows. Because of the mirror plane, fluoranthene **4** has two positions in which trifluoromethylation according to the Togni protocol can occur. The sterically demanding methyl group may inhibit *ortho* attack and, indeed, after slight modification of the reaction conditions, 1,6,7,10-tetramethyl-3,8,9-tris(trifluoromethyl)fluoranthene (**5**) could be isolated from the reaction mixture by column chromatography on silica gel in 36% yield in high purity (Scheme 3).



Scheme 3. Synthesis of substituted fluoranthenes **4** and **5**. a) Pentan-3-one (5.5 equiv), KOH (1.65 equiv), MeOH, 1 h, RT, then hexafluorobutyne (3.9 equiv), Ac<sub>2</sub>O, 60 °C, 48 h; b) 1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (Togni's acid reagent, 1.75 equiv), methyltrioxorhenium (0.1 equiv), 1,2-dichloroethane, 80 °C, 12 h.

The corresponding tris(trifluoromethyl)corannulene **11** was again obtained, in 16% yield, but so far no single crystals suitable for X-ray analysis could be grown.

To obtain further and higher trifluoromethylated corannulenes, the fluoranthene **5** can be treated again by the afore-



Scheme 4. Subsequent trifluoromethylation of **5** yields two regioisomers in a ratio of 2.3:1 (*asym-6*:*sym-6*). a) 1-Trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (Togni's acid reagent, 1.75 equiv), methyltrioxorhenium (0.1 equiv), 1,2-dichloroethane, 80 °C, 8 h, total yield 44%.

mentioned trifluoromethylation protocol (Scheme 4). In this case, however, a mixture of trifluoromethylated products was obtained in a 6:2:1 ratio (**5**:*asym-6*:*sym-6*), which could be separated by recycling HPLC giving *sym-6*, *asym-6* and **5** (in order of elution). Judging from the <sup>19</sup>F NMR spectrum the C<sub>1</sub>-symmetrical (one broad signal at –52.88 and two sharp singlets at –57.90 and –60.13 ppm in a 2:1:1 ratio) *asym-6* and the C<sub>2</sub>-symmetrical compound (two singlets in the <sup>19</sup>F NMR spectrum at –52.94 –55.08 ppm in a ratio of 1:1) *sym-6* were unambiguously identified. Both fluoranthenes were accumulated and subjected to the ring-closing protocol, which yielded the desired corannulene only in the case of *sym-6*, to form 1,2,6,7-tetrakis(trifluoromethyl)corannulene (**12**).

Probably due to severe molecular strain (as apparent (di)bromination of the sterically highly stressed methyl groups might be unfavourable), fluoranthene *asym-6* did not undergo the desired ring-closing reaction, whereas *sym-6* did, albeit with very low yield.

To obtain access to functionalized trifluoromethylated corannulenes, the sodium hydroxide mediated ring-closing conditions of Sygula, Rabideau et al.<sup>[32a,b]</sup> were applied successfully. Like tetrabromocorannulene, the insolubility of 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene (**8**) in common organic solvents prohibited the acquisition of <sup>13</sup>C NMR data,<sup>[32b]</sup> but the compound can be identified from <sup>1</sup>H and <sup>19</sup>F NMR data due its C<sub>s</sub> symmetry. A broad singlet for the six equivalent fluorine atoms is observed in the <sup>19</sup>F NMR spectrum at –49.96 ppm, and a singlet for the hydrogen atoms in *ortho* positions to the bromine atoms and an AB-type pattern for the remaining hydrogen atoms on the corannulene molecule in the <sup>1</sup>H NMR spectrum.

Instead of hexafluorobutyne or cyclic maleimides,<sup>[26b,34]</sup> bis(pentafluorophenyl)acetylene (**14**)<sup>[35]</sup> can be prepared and was used in the same manner to synthesize *ortho*-bis(pentafluorophenylated) fluoranthene **7** in 54% yield. Depending on the choice of reaction conditions, as described previously, 1,2-bis(pentafluorophenyl)corannulene (**13**) or 4,9-dibromo-1,2-bis(pentafluorophenyl)corannulene (**9**) can be obtained in 36 or 52% yield, respectively. Dibromocorannulene **9** can, for example, be methylated<sup>[31b,32b]</sup> to yield 4,9-dimethyl-1,2-bis(pentafluorophenyl)corannulene (**15**), the improved solubility of which in comparison to the brominated starting material gave access to satisfactory <sup>13</sup>C NMR data. The rota-

tion of the pentafluorophenyl groups is fast and unrestricted on the NMR timescale at room temperature for all three studied compounds, and in each case in an AA'BB'C-type  $^{19}\text{F}$  NMR spectrum results. The chemical shift is not dependent on other substituents attached to the corannulene bowl, and for all pentafluorophenyl rings multiplets at  $-137$ ,  $-152$  and  $-160$  ppm are observed in  $\text{CDCl}_3$ , corresponding to the *ortho*-, *para*- and *meta*-fluorine atoms, respectively.

**Crystal structures:** A surprising discovery was made during the purification of **2**, namely, its co-crystallization with pristine corannulene **1**. Mixtures containing variable amounts of **1** and **2** have a needle-like appearance after removal of the solvent, whereas pure corannulene appears as block-like crystals. Satisfactory X-ray data could not be obtained for mixed crystals due to severe disorder. This finding, however, is in accord with the results of Scott et al., who showed that several corannulenes undergo complexation reactions with equimolar quantities of perfluoro-*ortho*-phenylenemercury to yield extended binary stacks in which the molecules alternate.<sup>[36]</sup>

Slow evaporation of a pentane/dichloromethane solution furnished pale needle-like crystals of pure **2**, which could be solved in the monoclinic space group  $P2_1/c$ , whereby the fluorine atom is disordered over two positions in the solid state (1,4-positions). Crystallographic data of **2** are listed in Table 1. The bowl depth of **2** is only slightly shallower

Table 1. X-ray crystallographic details of studied compounds.

| Compound                                | <b>2</b>                          | <b>8</b>                                       | <b>16</b>                          |
|---|-----------------------------------|--|------------------------------------|
| formula                                 | $\text{C}_{20}\text{H}_9\text{F}$ | $\text{C}_{22}\text{H}_6\text{Br}_2\text{F}_6$ | $\text{C}_{20}\text{H}_9\text{Cl}$ |
| mass                                    | 268.27                            | 544.09   | 284.72                             |
| crystal system                          | monoclinic                        | monoclinic                                     | orthorhombic                       |
| space group                             | $P2_1/c$                          | $P2_1/c$                                       | $Pnma$                             |
| $a$ [Å]                                 | 17.700(7)                         | 18.9513(6)                                     | 7.341(3)                           |
| $b$ [Å]                                 | 9.540(4)                          | 12.3654(4)                                     | 18.116(7)                          |
| $c$ [Å]                                 | 7.308(3)                          | 7.3171(3)                                      | 9.533(4)                           |
| $\alpha$ [°]                            | 90                                | 97.040(1)                                      | 90                                 |
| $\beta$ [°]                             | 90.063(9)                         | 90   | 90                                 |
| $\gamma$ [°]                            | 90                                | 90   | 90                                 |
| $V$ [Å <sup>3</sup> ]                   | 1234.0(9)                         | 1701.76(10)                                    | 1267.8(9)                          |
| $T$ [K]                                 | 100(2)                            | 100.0(2)                                       | 133(2)                             |
| $Z$                                     | 4                                 | 4  | 4                                  |
| total reflns                            | 11020                             | 13550  | 11263                              |
| unique reflns                           | 11020                             | 3109   | 1155                               |
| $R_{\text{int}}$                        | 0.0000                            | 0.0413   | 0.0374                             |
| final $R_1$ values [ $I > 2\sigma(I)$ ] | 0.0665                            | 0.0279   | 0.0797                             |
| final $wR(F^2)$ values (all data)       | 0.1804                            | 0.0680   | 0.1974                             |
| GOF on $F^2$                            | 1.057                             | 1.055  | 1.165                              |

(0.87 Å) than that of corannulene (0.88 Å)<sup>[39]</sup> and consequently deeper than that of **8** (0.79 Å). The solid-state structure is drastically changed upon introduction of the strongly electron withdrawing fluorine atom on the corannulene rim. Within one strand, along the crystallographic  $c$  axis, the bowl direction is the same, but the molecular bowls are not only displaced, but also twisted by  $180^\circ$ , so that an overall slipped stacking motif results (see Figure 1).<sup>[40]</sup> A short

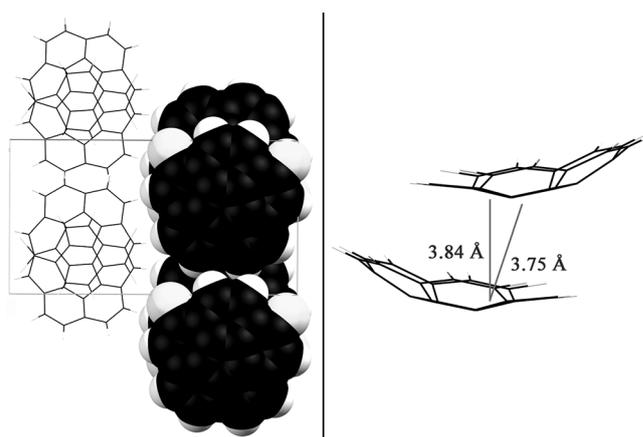


Figure 1. Mercury<sup>[37]</sup> representation rendered with POV-Ray<sup>[38]</sup> of the molecular structure and packing diagram of **2** determined by single-crystal X-ray diffraction (carbon black, fluorine light grey, hydrogen white). Left: View along the crystallographic  $a$  axis. Right: An excerpt showing two interacting bowls. The bowl depth was found to be 0.8658(3) Å. Note the offset stacking of the molecular bowls and the disorder of the fluorine atom at two positions (equally occupied).

$\text{CH}\cdots\pi$  interaction<sup>[41]</sup> of 2.86 Å can be observed from one of the CH rim atoms to the centre of a proximate six-membered ring of the corannulene pointing in the same direction. This occurs within unidirectional columns, whereas the opposing columns participate predominantly by an intermolecular  $\text{F}\cdots\text{HC}$  interaction<sup>[24a,42]</sup> of 2.66 Å yielding the overall solid-state alignment. The shortest centroid-to-centroid distances within one strand are 3.84 Å for two opposing six-membered rings and 3.75 Å for a six-membered ring in contact with a central five-membered ring.

For comparison, the homologous monochlorocorannulene (**16**) was also investigated by X-ray crystallography. The solid-state structure of a needle-like crystal of **16** shows an almost identical packing structure, despite a change of the space group (orthorhombic space group  $Pnma$ ) and again disorder of the chlorine atoms at the 1- and 4-positions.<sup>[43]</sup> Therefore, it can be concluded that the packing structure is formed mainly because of electrostatic interactions and not due to  $\text{F}\cdots\text{HC}$  interactions. Crystallographic data of **16** are listed in Table 1.

Slow evaporation of a pentane/dichloromethane solution furnished pale yellow needle-like crystals of 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene (**8**) that were suitable for X-ray analysis, the structure of which was solved in the monoclinic space group  $P2_1/c$  (Figure 2). Crystallographic data of **8** are listed in Table 1. The increased substitution along the corannulene rim flattens the bowl to 0.79 Å (0.88 Å in the case of ten hydrogen atoms on the corannulene rim and 0.82 Å for the bis-trifluoromethylated **10** and decreases the intermolecular  $\pi\cdots\pi$  stacking distance further to 3.67 Å (hub-to-hub centroid distance of 3.73 Å for the un-brominated **10**). Within one strand along the crystallographic  $c$  axis, the bowl direction is the same and the molecular bowls are slightly tilted with respect to the stacking axis by  $6.9^\circ$  (the angle between the hub plane and the  $ab$  plane).

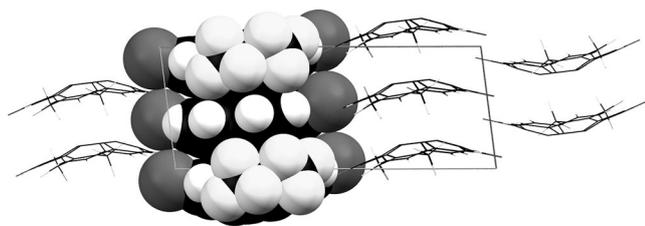


Figure 2. Mercury<sup>[37]</sup> representation rendered with POV-Ray<sup>[38]</sup> of the molecular structure and packing diagram of **8** determined by single-crystal X-ray diffraction (carbon black, bromine dark grey, fluorine light grey, hydrogen white), viewed along the crystallographic *b* axis. The bowl depth was found to be 0.7949(0) Å, with a bowl-to-bowl distance of 3.725(1) Å, as obtained from the hub-to-hub centroid distance.

The bowls are not superimposed, the central five-membered ring deviates slightly by approximately 13° and the substituents are rotated by about 140°, probably to maximize both the electrostatic interactions between two stacked bowls and intercolumnar hydrogen bonding.

The antiparallel molecular strands are engaged in a few CH...F contacts of about 2.73 Å, and no rotational disorder of the trifluoromethyl group is observed. The hydrogen bonding in this crystal is dominated by CH...Br contacts with distances of 2.96–3.24 Å, connecting the molecular columns, in accordance with the common sense of the strength of halogens participating in halogen bonding.<sup>[44]</sup> Overall a dense columnar packing is found, like that observed for **8** and 1,2,5,6-tetrabromocorannulene,<sup>[40]</sup> whereby the molecular bowl is flattened because of the steric demand of the increasing number of substituents.<sup>[45]</sup>

Control of the solid-state packing of the molecular bowls is inherently important,<sup>[46]</sup> because we have shown that unsubstituted corannulene, with its non-columnar stacking, has only very limited conductivity. Substituted corannulene **10**, with its perfect columnar arrangement, shows a 1000-fold higher conductivity.<sup>[26c]</sup>

**Electrochemistry:** To study the electron-acceptor abilities of the new corannulenes, cyclic voltammetry and square-wave measurements (if available) were conducted. The experiments were conducted in THF or CH<sub>2</sub>Cl<sub>2</sub>, and all potentials were referenced against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (internal standard). To achieve oxidation of a sample, usually a solvent like acetonitrile with a broad anodic window is used, but most samples of this study were (almost) insoluble and did not give satisfying measurements.

For one substituent, calculated and experimental data match within the range of error for fluoro, chloro and trifluoromethyl groups (Figure 3). For higher numbers of substituents, deviations are apparent. This may not be attributable to inaccurate calculations, but to a significant dependence of the electron affinities on the substitution pattern on the corannulene rim. The calculated substitution patterns are given in the legend to Figure 3. Probably, **10** is a stronger electron acceptor than 1,5-bis(trifluoromethyl)corannulene and maybe even the strongest electron acceptor of all

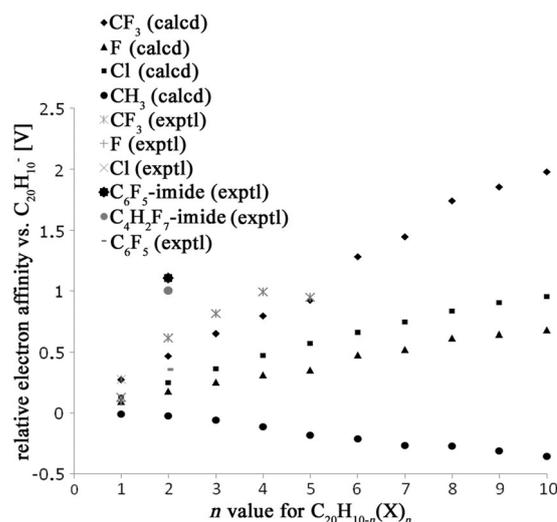


Figure 3. Electron affinities relative to corannulene plotted against the number of substituents on the rim. A comprehensive comparison of experimentally obtained data in this work, except for CF<sub>3</sub> with *n* = 5, which is an experimental value but taken from Petrukhina et al.<sup>[25]</sup> The calculated data were taken from ref. [25]: Calculated substitution patterns for *n* = 2 (1,5), *n* = 3 (1,3,7), *n* = 4 (1,3,5,7) and *n* = 5 (1,3,5,7,9), because significant variation of electron affinities were not expected if the added groups are distributed more or less uniformly. Several methylated corannulenes were also investigated electrochemically by Siegel and co-workers.<sup>[31b]</sup>

bis-trifluoromethylated corannulenes, because the two trifluoromethyl groups in immediate proximity lead to a highly polarized π system. In general, after the introduction of one trifluoromethyl group (**3**), the *E*<sub>1/2</sub> value of the reduction is shifted by 0.28 V towards higher potentials relative to corannulene **1**. For pentakis(trifluoromethyl)corannulene, Petrukhina and co-workers observed a shift of 0.95 V,<sup>[25]</sup> which roughly corresponds to a shift of 0.19 V per trifluoromethyl group. Through selective substitution in specific positions and the resulting lower symmetry, this shift can be increased to 0.25 V per trifluoromethyl group on average. Because of the different substitution pattern, no strictly linear increase of the electron accepting ability can be expected. For corannulene **11** with three trifluoromethyl groups, and for **12** with four, shifts of 0.82 and 1.0 V are observed relative to **1**; these shifts surpass that of pentakis(trifluoromethyl)corannulenes (0.95 V).

The influence of pentafluorophenyl groups was not considered before. In the case of **13**, the effect of the pentafluorophenyl substituent on the electron affinity is less pronounced than that of trifluoromethyl group but still superior to that of a chloro substituent. In general, the influence on electron affinity of the studied substituents follow the rough order of CF<sub>3</sub> > C<sub>6</sub>F<sub>5</sub> > Cl > F, which is surprising at first sight. Fluorine, having the highest electronegativity of all elements, induces a strongly polarized C–F single bond and thus results in a dipole moment along the C–F bond axis. Fluorine is a strong σ acceptor and, to some extent, a π donor. The trifluoromethyl substituent is both a strong σ and π acceptor and induces a stronger dipole moment than

just one fluorine atom.<sup>[47]</sup> For  $\alpha,\beta$ -unsaturated systems, this phenomenon is known (negative hyperconjugation), and it may be a possibility to explain the experimentally obtained values as well.

Fluorine atoms have a much smaller effect than  $\text{CF}_3$  groups and a smaller effect than chlorine atoms, contrary to the results for  $\text{C}_{60}\text{F}_n$  versus  $\text{C}_{60}(\text{CF}_3)_n$ .<sup>[48]</sup> The difference may be due to the different substituents on  $\text{sp}^2$  carbon atoms in conjugation with an extensive  $\pi$  system in corannulene and substituents on  $\text{sp}^3$  carbon atoms, like in fluorinated fullerenes. Density functional calculations further revealed that addition patterns with double bonds in five-membered rings having two  $\text{sp}^2$  neighbours result in the strongest electron acceptors.<sup>[48]</sup> This offers an explanation of why the studied corannulenes bearing two trifluoromethyl groups in *ortho* positions are even stronger electron-acceptor molecules than the isomers used in calculations,<sup>[25]</sup> despite a possible solvent effect.

The earlier reported cyclic imides were added to Figure 3 with a substituent count of two on the corannulene rim and show the strongest change. However, the first reduction wave to the monoanion is expected to take place at the extended node of the molecules, which would be the highly conjugated five-membered imide ring and not the corannulene framework itself.

## Conclusion

Fluorinated and trifluoromethylated corannulenes have been prepared by liquid-phase synthesis. Corannulenes with up to four trifluoromethyl groups or one fluoro substituent have been isolated and characterized. X-ray crystallographic analyses revealed a columnar packing for the dibrominated and bis-trifluoromethylated corannulene and a slipped stacking motif for fluorocorannulene. Deeper understanding of the intrinsic properties of corannulenes bearing electron-withdrawing groups were obtained by analyzing their electrochemical behaviour in THF solution. A strong dependence on the substitution pattern is suggested to explain the difference between calculated and experimentally observed electron acceptor strength.

## Experimental Section

**Techniques:** All experiments were carried out by standard Schlenk methods under argon atmosphere or by working in an argon-filled MBraun glove box model LABmaster SP or a nitrogen-filled MBraun glove box model UNIlab 2000.

**Chemicals:** Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to use and further purified by trap-to-trap distillation for electrochemical use, 1,2-dichloroethane and *N,N*-dimethylformamide were distilled from phosphorus pentoxide and stored over molecular sieves (3 Å) or purchased in anhydrous form and used as received. Dichloromethane was dried over activated alumina by using an MBraun solvent system model MB SPS-800 or Glass Contour solvent purification system. Anhydrous methanol was purchased and used as received. Nickel powder (99.5%, 150  $\mu\text{m}$ ), gold(III) chloride and hexafluorobutene were

obtained from ABCR, methyltrioxorhenium(VII) from ABCR or TCI, *N*-iodosuccinimide from Molekula, *N*-bromosuccinimide and pentan-3-one from Acros Organics, 2,2'-azobisisobutyronitrile (AIBN) from TCI and dibenzoyl peroxide (DBPO) from Alfa Aesar. Diiodoacetylene (**17**)<sup>[35a]</sup> and bis(pentafluorophenyl)acetylene (**14**)<sup>[35b]</sup> were synthesized by literature procedures. Compounds **14**, **17** and Togni's Reagent should be handled with special care due to their toxicity and explosive nature.<sup>[29b]</sup> Xenon difluoride was obtained from the elements<sup>[49]</sup> or purchased from Sigma-Aldrich. 1-Trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one was synthesized by a literature procedure starting from 2-iodobenzoic acid<sup>[29b]</sup> or purchased from TCI. Corannulene (IUPAC: dibenzo-[*ghi,mno*]fluoranthene) (**1**)<sup>[31a]</sup> was synthesized according to previously published methods.

CCDC-939699 (**2**), CCDC-939697 (**8**), and CCDC-939698 (**16**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**Instrumentation:** Melting points were determined on a Gallenkamp Melting Point Apparatus or Stanford Research Systems MPA100 and are uncorrected. IR spectra were recorded on a Nicolet 5 SXC FTIR spectrometer equipped with a DTGS detector or on a JASCO FT IR-4100 spectrometer.  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL ECS 400/500 spectrometer or on a Bruker Instruments AVIII 700 at 23 °C.  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  were used as solvents, if not stated otherwise, and the residual solvent peak was taken as internal standard ( $^1\text{H}$  NMR:  $\text{CDCl}_3$  7.26,  $\text{CD}_2\text{Cl}_2$  5.30 ppm;  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  77.0 ppm,  $\text{CD}_2\text{Cl}_2$  54.0 ppm; always proton-decoupled). Chemical shifts are reported in parts per million ( $\delta$ ) relative to TMS.  $^{19}\text{F}$  NMR spectra were referenced against external  $\text{CFCl}_3$ . Mass spectra were measured on a MAT CH7A (EI, 80 eV, 3 kV) at the given temperature for each sample or on a JEOL JMS-777V. High-resolution masses were determined by peak-match method against perfluorokerosene. Gel permeation chromatography (GPC) was performed on JAIGEL 1H and 2H by using a JAI Recycling Preparative HPLC LC-908W and chloroform as eluent. HPLC analysis and separation were performed with a JASCO LC-2000 HPLC using Cosmosil Buckyprep columns. TLC (precoated) analysis and PTLC (precoated and self-made) was performed using Merck silica gel 60 F<sub>254</sub> or Wako Wako-gel B-5F. Some reactions were carried out in personal parallel chemical reactors (EYELA Chemistation series) and low-temperature reactors (EYELA PSL series).

Single-crystal X-ray structure determination was performed on a Bruker-AXS SMART 1000 fitted with a CCD; the crystal of compound **8** was studied on a Bruker D8 QUEST. Data collection, reduction and empirical absorption correction were performed with the SMART, SAINT and SADABS programs, respectively;<sup>[50]</sup> the SHELX program package<sup>[51]</sup> was used for structure solution and refinement.

**Monofluorocorannulene (2):** Corannulene (**1**; 98.8 mg, 0.39 mmol, 1.0 equiv) was dissolved in dichloromethane (5 mL) and the solution cooled to  $-78^\circ\text{C}$ . Solid xenon difluoride (92.0 mg, 0.54 mmol, 1.38 equiv) was added at once and the flask was sealed again. The mixture was allowed to warm to room temperature over 3 h. The green slurry was diluted with 30 mL of dichloromethane and silica gel was added. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (pentane/ethyl acetate 20/1) to yield **2** together with unconverted corannulene and small amounts of the regioisomers of  $\text{C}_{20}\text{H}_8\text{F}_2$  (as indicated by a series of doublets between  $-116$  and  $-119$  ppm exhibiting  $^3J(\text{H},\text{F})$  coupling constants of  $\approx 13$  Hz) as an amorphous powder (34% conversion by crude NMR). Compound **2** was further purified by RP-HPLC to give analytically pure **2** (Gemini C18, methanol/water 9/1) at a flow rate of  $1\text{ mL}\cdot\text{min}^{-1}$  and 148 bar with an  $R_t$  value of 10.9 min. M.p.  $226^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.39$  (d,  $^3J(\text{F},\text{H}) = 13$  Hz, 1H), 7.78–7.88 (m, 7H), 7.96 (d,  $1/2$  AB,  $^3J(\text{H},\text{H}) = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 160.00$  (d,  $^1J(\text{C},\text{F}) = 260$  Hz, 1C; CF), 135.53 (d,  $J(\text{C},\text{F}) = 9$  Hz, 1C;  $\text{C}_{\text{hub}}$ ), 136.21 (s, 1C;  $\text{C}_{\text{hub}}$ ), 135.38 (s, 1C;  $\text{C}_{\text{hub}}$ ), 134.80 (d,  $J(\text{C},\text{F}) = 5$  Hz, 1C;  $\text{C}_{\text{hub}}$ ), 132.70 (s, 1C;  $\text{C}_{\text{flank}}$ ), 132.16 (d,  $J(\text{C},\text{F}) = 10$  Hz, 1C;  $\text{C}_{\text{flank}}$ ), 131.11 (s, 1C;  $\text{C}_{\text{flank}}$ ), 130.87 (s, 1C;  $\text{C}_{\text{flank}}$ ), 130.28 (s, 1C;  $\text{C}_{\text{flank}}$ ), 127.85 (s, 1C;  $\text{C}_{\text{rim}}$ ), 127.78 (s, 1C;  $\text{C}_{\text{rim}}$ ), 127.51 (s, 1C;  $\text{C}_{\text{rim}}$ ), 127.26 (s, 1C;  $\text{C}_{\text{rim}}$ ), 127.02 (s, 1C;  $\text{C}_{\text{rim}}$ ), 126.71 (d,  $^3J$ -

(C,F)=4 Hz, 1C;  $C_{\text{rim}}$ : 126.64 (s, 1C;  $C_{\text{rim}}$ ), 121.80 (d,  $^2J(\text{C,F})=22$  Hz, 1C), 112.36 (s, 1C), 109.83 (d,  $^2J(\text{C,F})=109.8$  Hz, 1C);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta=-118.3$  (d,  $^3J(\text{F,H})=13$  Hz, 1F); IR:  $\tilde{\nu}=2921$  (m), 2845 (m), 1620 (s), 1438 (s), 1376 (s), 1108 (s), 997 (m), 824 (m), 566  $\text{cm}^{-1}$  (m); MS (EI):  $m/z$  (%): 268 (100)  $[\text{M}]^+$ , 134 (15)  $[\text{M}]^{2+}$ ; HRMS (EI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_6\text{F}$ : 268.0688; found: 268.0677.

**1,6,7,10-Tetramethyl-3,4,8,9-tetrakis(trifluoromethyl)fluoranthene (sym-6) and 1,6,7,10-tetramethyl-2,4,8,9-tetrakis(trifluoromethyl)fluoranthene (asym-6)**: 1,6,7,10-Tetramethyl-3,8,9-tris(trifluoromethyl)fluoranthene (**13**; 67.4 mg, 0.15 mmol, 1.00 equiv), methyltrioxorhenium (3.6 mg, 0.015 mmol, 0.10 equiv), and 1-(trifluoromethyl)-1,2-benziodoxol-3(1H)-one (81.0 mg, 0.26 mmol, 1.75 equiv) were charged into a flame-dried Schlenk tube and dissolved in 4 mL of absolute 1,2-dichloroethane. The reaction mixture was stirred at 80 °C for 12 h under an argon atmosphere. During the first 60 min, the colour turned from yellow to black. The solvent was evaporated and the crude product was prepurified by filtration through a short silica-gel plug with *n*-pentane/dichloromethane (1/1). The crude product (consisting of a mixture of *sym-6*, *asym-6* and the starting material) was subjected to purification by GPC (eight cycles on average) to yield the products *asym-6* (23.6 mg, 31%) and *sym-6* (9.9 mg, 13%) as well as remaining starting material **5** (21.9 mg, 32%) as a pale yellow solids.

Data for *asym-6*: Yield: 31%; m.p. 153 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.46$  (s, 1H), 7.83 (s, 1H), 2.82 (s, 3H), 2.80–2.75 (m, 6H), 2.74–2.69 ppm (m, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta=144.35$  (s, 1C), 143.56 (s, 1C), 137.37 (s, 1C), 137.09 (s, 1C), 136.51 (s, 1C), 135.67 (s, 1C; CH), 133.30 (s, 1C), 132.30–130.58 (m, 1C; C-CF<sub>3</sub>), 132.17 (s, 1C; CH), 128.48–127.06 (m, 2C; CCF<sub>3</sub>), 126.04 (s, 1C; CCH<sub>3</sub>), 124.89–124.71 (m, 1C; CCF<sub>3</sub>), 124.79 (s, 1C), 124.10 (s, 1C; CCH<sub>3</sub>), 123.57 (s, 1C, CCH<sub>3</sub>), 126.63 (s, 1C; CCH<sub>3</sub>), 25.68 (brs, 2C; CH<sub>3</sub>), 23.46–23.32 (m, 1C; CH<sub>3</sub>), 21.30 ppm (q,  $J(\text{C,F})=3.0$  Hz; CH<sub>3</sub>), the CF<sub>3</sub> carbon atoms could not be assigned due to strong coupling with large coupling constants and the consequent low S/N ratios;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta=-52.88$  (brs, 6F), -57.90 (s, 3F), -60.13 ppm (s, 3F); IR:  $\tilde{\nu}=2994$  (w), 2967 (w), 1469 (w), 1372 (w), 1344 (m), 1280 (s), 1207 (m), 1109 (s), 1051 (s), 990 (m), 916 (m), 742  $\text{cm}^{-1}$  (m); MS (EI):  $m/z$  (%): 530 (100)  $[\text{M}]^+$ , 515 (30)  $[\text{M}-\text{CH}_3]^+$ , 461 (25)  $[\text{M}-\text{CF}_3]^+$ ; HRMS (EI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{14}\text{F}_{12}$ : 530.0904; found: 530.0906.

Data for *sym-6*: Yield: 13%; m.p. 198 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.00$  (s, 2H), 2.74 (s, 6H), 2.72 ppm (s, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta=143.14$  (s, 2C), 137.71 (s, 2C), 136.48 (s, 2C), 135.04 (s, 2C), 133.36 (s, 2CH), 131.50 (s, 2C), 118.64 (s, 1C), 24.04 (s, 2C; CH<sub>3</sub>), 22.29 ppm (s, 2C; CH<sub>3</sub>), CF<sub>3</sub> and the corresponding CCF<sub>3</sub> could not be observed due to strong coupling and the consequent low S/N ratios;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta=-52.94$  (s, 6F), -55.08 ppm (s, 6F); IR:  $\tilde{\nu}=3001$  (w), 2967 (w), 1604 (w), 1509 (w), 1472 (w), 1344 (m), 1280 (s), 1210 (s), 1115 (s), 1045 (s), 993 (s), 745 (m), 724  $\text{cm}^{-1}$  (m); MS (EI):  $m/z$  (%): 530 (100)  $[\text{M}]^+$ , 515 (15)  $[\text{M}-\text{CH}_3]^+$ , 461 (24)  $[\text{M}-\text{CF}_3]^+$ ; HRMS (EI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{14}\text{F}_{12}$ : 530.0904; found: 530.0903.

**1,6,7,10-Tetramethyl-8,9-bis(perfluorophenyl)fluoranthene (7)**: In a 50 mL Schlenk flask 3,8-dimethylacenaphthylene-1,2-dione (461 mg, 2.2 mmol, 1.0 equiv) and pentan-3-one (1.22 mL, 7.6 mmol, 3.5 equiv) were suspended in methanol (12 mL). A solution of potassium hydroxide (1 g, 17.8 mmol, 8.1 equiv) in methanol (5 mL) was added by syringe and the mixture was stirred for one hour at room temperature. The yellow solution was diluted with 50 mL of dichloromethane and extracted three times with 10% hydrochloric acid (50 mL). After drying with anhydrous sodium sulfate and quick removal of the solvent, the crude product was transferred to a 50 mL Schlenk tube and vacuum-dried. The vessel was purged with argon, and acetic anhydride (12 mL) and bis(pentafluorophenyl)acetylene (**14**) (1.1 g, 3.1 mmol, 1.4 equiv) were added in one portion. The dark brown solution was stirred at 110 °C for 6 d. The solvent of the cooled reaction mixture was evaporated, and the dark solid residue was purified by column chromatography on silica gel (pentane/dichloromethane 10/1). The product was obtained as a yellow-green solid 698 mg (54%). Unconverted **14** (584 mg) could be recovered from the first (colourless) fraction. Yield: 54%; m.p. 216 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.77$  (d,  $^1/2$  AB,  $^3J(\text{H,H})=8.2$  Hz, 2H), 7.42 (d,  $^1/2$  AB,  $^3J(\text{H,H})=$

8.2 Hz, 2H), 2.82 (s, 6H), 2.46 ppm (s, 6H);  $^{13}\text{C}\{^1\text{H},^{19}\text{F}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta=144.22$  (s, 4C; CF), 142.24 (s, 2C; CF), 140.94 (s, 4C; CF), 137.53 (s, 2C), 133.75 (s, 1C), 133.67 (s, 2C), 133.43 (s, 2C), 131.95 (s, 2C; CH), 129.79 (s, 2C), 127.33 (s, 2C; CH), 126.74 (s, 2C), 126.66 (s, 1C), 114.34 (s, 2C), 24.83 (s, 2C), 21.85 ppm (s, 2C);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): AA'BB'C-type  $\delta=-138.6$ –138.8 (m, 4F; *ortho*), -152.9–153.1 (m, 2F; *para*), -161.0–161.2 ppm (m, 4F; *meta*); IR:  $\tilde{\nu}=3063$  (w), 2949 (w), 1713 (s), 1520 (s), 1496 (s), 1434 (s), 1410 (s), 1376 (m), 1107 (m), 980 (s), 897 (s), 790 (s), 735  $\text{cm}^{-1}$  (m); MS (EI, 130 °C):  $m/z$  (%): 590 (100)  $[\text{M}]^+$ , 575 (37)  $[\text{M}-\text{CH}_3]^+$ ; HRMS (EI, 130 °C):  $m/z$  calcd for  $\text{C}_{32}\text{H}_{16}\text{F}_{10}$ : 510.1092; found: 590.1103.

**General procedure for the synthesis of 1,2-disubstituted corannulenes (12, 13)**: For reaction times, solvent and reagent quantities for each compound, see the Supporting Information; for the preparation of **10** and **11**, see ref. [22b]. In a 100 mL round-bottom flask, the corresponding fluoranthene **4–7** was dissolved in tetrachloromethane. *N*-Bromosuccinimide and 3% AIBN or DBPO were added and the suspension was heated to reflux for the given time while irradiating with a 150 W sunlight lamp. The reaction mixture was cooled and all volatile materials were removed under reduced pressure. The solid residue was (partially) redissolved in dichloromethane and extracted with water. After drying with anhydrous sodium sulfate and removal of the solvent, the crude product was transferred to a small Schlenk tube and vacuum-dried. A brown suspension formed upon addition of nickel powder and anhydrous DMF, which was heated to 80 °C in the closed vessel for the given time. The reaction was stopped by addition of water, and the crude product was transferred to a separation funnel. Dichloromethane was added and the organic layer was washed with water. After drying with anhydrous sodium sulfate, the product was finally purified by column chromatography on silica gel and, if necessary, GPC. All compounds were isolated as pale yellow solids.

Data for 1,2,6,7-tetrakis(trifluoromethyl)corannulene (**12**): Yield: 11%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.57$  (s, 2H), 8.35–8.27 (m,  $^1/2$  AB, 2H), 8.31 (d,  $^1/2$  AB,  $^3J(\text{H,H})=9.2$  Hz, 2H), 8.02 ppm (d,  $^3J(\text{H,H})=9.2$  Hz, 2H), the peaks of the downfield part of the AB signal show weak  $^{19}\text{F}$  couplings;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta=-50.46$  (s, 6F; CF<sub>3</sub>) -56.20 ppm (s, 6F; CF<sub>3</sub>); MS (EI):  $m/z$  (%): 522 (100)  $[\text{M}]^+$ , 502 (20)  $[\text{M}-\text{F}]^+$ , 453 (25)  $[\text{M}-\text{CF}_3]^+$ ; HRMS (EI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_6\text{F}_{12}$ : 522.0278; found: 522.0273.

Data for 1,2-bis(pentafluorophenyl)corannulene (**13**): Yield: 36%; m.p. 231 °C;  $^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ ):  $\delta=7.89$  (d,  $^1/2$  AB,  $^3J(\text{H,H})=8.8$  Hz, 2H), 7.86 (d,  $^1/2$  AB,  $^3J(\text{H,H})=8.9$  Hz, 2H), 7.85 (d,  $^1/2$  AB,  $^3J(\text{H,H})=8.7$  Hz, 2H), 7.39 ppm (d,  $^1/2$  AB,  $^3J(\text{H,H})=8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ ):  $\delta=145.54$ –143.35 (m, 4C; CF), 142.50–140.15 (m, 2C; CF), 138.69–136.56 (m, 4C; CF), 136.52 (s, 1C;  $C_{\text{hub}}$ ), 135.50 (s, 2C;  $C_{\text{hub}}$ ), 135.41 (s, 2C;  $C_{\text{hub}}$ ), 131.50 (s, 2C;  $C_{\text{flank}}$ ), 131.42 (s, 1C;  $C_{\text{flank}}$ ), 128.76 (s, 2C;  $C_{\text{flank}}$ ), 128.55 (s, 2C;  $C_{\text{rim}}$ ), 128.25 (s, 2C;  $C_{\text{rim}}$ ), 127.39 (s, 2C;  $C_{\text{rim}}$ ), 125.88 (s, 2C;  $C_{\text{ipso}}$ ), 124.96 (s, 2C;  $C_{\text{rim}}$ ), 111.61 ppm (t,  $^2J(\text{C,F})=17.1$  Hz, 2C;  $C_{\text{ipso}}$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ): AA'BB'C-type  $\delta=-137.65$ –137.90 (m, 4F; *ortho*), -151.48–151.70 (m, 2F; *para*), -160.20–160.45 ppm (m, 4F; *meta*); IR:  $\tilde{\nu}=3039$  (w), 1648 (m), 1520 (s), 1486 (s), 1300 (w), 1107 (m), 1079 (m), 983 (s), 952 (s), 904 (w), 818 (s), 735 (m), 700 (m), 563  $\text{cm}^{-1}$  (m); MS (EI, 100 °C):  $m/z$  (%): 582 (100)  $[\text{M}]^+$ , 562 (21)  $[\text{M}-\text{HF}]^+$ , 542 (10)  $[\text{M}-2\text{HF}]^+$ , 291 (4)  $[\text{M}]^{2+}$ ; HRMS (EI, 100 °C):  $m/z$  calcd for  $\text{C}_{32}\text{H}_8\text{F}_{10}$ : 582.0466; found: 582.0450.

**General procedure for the synthesis of 1,2-disubstituted corannulenes carrying two bromo substituents in the 4,9-positions (8, 9)**: For reaction times, solvent and reagent quantities for each compound, see the Supporting Information. In a 100 mL round-bottom flask, the corresponding fluoranthene **4** or **7** was dissolved in tetrachloromethane. *N*-Bromosuccinimide and 3% DBPO or AIBN were added, and the suspension was heated to reflux for the given time while irradiating with a 150 W sunlight lamp. The reaction mixture was cooled and all volatile materials were removed under reduced pressure. The solid residue was (partially) redissolved in dichloromethane and extracted with water. After drying with anhydrous sodium sulfate and removal of the solvent the crude product was transferred to a flask and dissolved in 1,4-dioxane/water (12/5). Sodium hydroxide pellets were added and the resulting suspension was heated to reflux for 20 min at 110 °C. After cooling to room tempera-

ture, the suspension was poured into water acidified with aqueous hydrochloric acid and the precipitate was filtered off under reduced pressure. The precipitate was dried under high vacuum and finally obtained as a brown solid, insoluble in most organic solvents.

Data for 4,9-dibromo-1,2-bis(trifluoromethyl)corannulene (**8**): Yield: 78%; m.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, 1,1,2,2-[D<sub>2</sub>]tetrachloroethane): δ = 8.34 (s, 2H), 8.00 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.9 Hz, 2H), 7.97 ppm (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.9 Hz, 2H); <sup>19</sup>F NMR (376 MHz, 1,1,2,2-[D<sub>2</sub>]tetrachloroethane): δ = -49.96 ppm (s, 6F; CF<sub>3</sub>); IR: ν̄ = 2959 (w), 2925 (w), 2854 (w), 1728 (w), 1658 (w), 1617 (w), 1577 (w), 1493 (w), 1442 (w), 1404 (w), 1348 (w), 1296 (m), 1258 (s), 1222 (m), 1155 (s), 1058 (m), 1015 (m), 933 (w), 903 (w), 865 (m), 747 (m), 736 (w), 660 (w), 624 (w), 564 (m), 533 cm<sup>-1</sup> (m); MS (EI, 150 °C): *m/z* (%): 541 (100) [M]<sup>+</sup>, 465 (24) [M-CF<sub>3</sub>]<sup>+</sup>, 334 (21), 315 (25) [M-2HBr-CF<sub>3</sub>]<sup>+</sup>, 167 (17); 157 (24) [M-2HBr-CF<sub>3</sub>]<sup>2+</sup>; HRMS (EI): *m/z* calcd for C<sub>22</sub>H<sub>6</sub>Br<sub>2</sub>F<sub>6</sub>: 541.8740; found: 541.8764.

Data for 4,9-dibromo-1,2-bis(pentafluorophenyl)corannulene (**9**): Yield: 52%; m.p. > 321 °C (gradually darkens); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.01–7.96 (m, 4H), 7.55 ppm (s, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): AA'BB'C-type: δ = -137.20–137.34 (m, 4F; *ortho*), -150.08–150.22 (m, 2F; *para*), -159.08–159.25 ppm (m, 4F; *meta*); IR: ν̄ = 2955 (w), 1717 (w), 1653 (m), 1524 (s), 1491 (s), 1112 (m), 1081 (w), 983 (s), 910 (m), 825 (w), 808 (w), 776 cm<sup>-1</sup> (w); MS (EI, 165 °C): *m/z* (%): 740 (100) [M]<sup>+</sup>, 660 (24) [M-Br]<sup>+</sup>, 580 (18) [M-2Br]<sup>+</sup>, 370 (10) [M]<sup>2+</sup>; HRMS (EI, 165 °C): *m/z* calcd for C<sub>32</sub>H<sub>6</sub>Br<sub>2</sub>F<sub>10</sub>: 737.8677; found: 737.8670.

**4,9-Dimethyl-1,2-bis(pentafluorophenyl)corannulene (**15**):** In a 50 mL Schlenk tube, bromide **9** (75 mg, 0.1 mmol, 1.0 equiv) was suspended in absolute 1,2-dimethoxyethane (8 mL). [NiCl<sub>2</sub>(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane; 5.5 mg, 0.01 mmol, 9.70 equiv) and a solution of trimethylaluminum in toluene (2 mol L<sup>-1</sup>, 0.5 mmol, 5 equiv) were added by syringe. The tube was sealed and the reaction mixture heated to 75 °C for 24 h. It was quenched by slow addition of ethanol with intense stirring while cooling with an ice bath. Dichloromethane was added and the mixture was extracted three times with 10% hydrochloric acid (50 mL), dried with anhydrous sodium sulfate and the solvent evaporated. The product was purified by column chromatography on silica gel (pentane/dichloromethane 10/1) and GPC separation with chloroform to yield the product as a colourless powder (18.5 mg). Yield: 30%; m.p. < 207 °C (gradually darkens); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>): δ = 7.97 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.8 Hz, 2H), 7.93 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.8 Hz, 2H), 7.28 (s, 2H), 2.82 ppm (s, 3H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>): δ = 145.54–143.79 (m, 4C; CF), 138.37 (s, 2C; C<sub>ipso</sub>), 136.17 (s, 1C; C<sub>hub</sub>), 135.54 (s, 2C; C<sub>hub</sub>), 134.62 (s, 2C; C<sub>hub</sub>), 131.80 (s, 2C; C<sub>flank</sub>), 130.84 (s, 1C; C<sub>flank</sub>), 138.96 (s, 2C; C<sub>flank</sub>), 128.14 (s, 2C; C<sub>rim</sub>), 125.48 (s, 2C; C<sub>ipso</sub>), 123.35 (s, 2C; C<sub>rim</sub>), 123.54 (s, 2C; C<sub>rim</sub>), 111.96 (t, <sup>2</sup>J(C,F) = 16.7 Hz, 2C; C<sub>ipso</sub>), 19.11 ppm (s, 2C; CH<sub>3</sub>); the other two CF signals could not be assigned due to strong coupling and consequent low S/N ratio; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): AA'BB'C type: δ = -137.41–138.39 (m, 4F; *ortho*), -150.47–153.00 (m, 2F; *para*), -159.97–161.29 ppm (m, 4F; *meta*); IR: ν̄ = 2971 (m), 2903 (m), 2848 (m), 2174 (s), 1653 (w), 1440 (s), 1369 (s), 1326 (s), 1026 (s), 979 (s), 813 (s), 722 (m), 683 cm<sup>-1</sup> (w); MS (EI, 120 °C): *m/z* (%): 610 (100) [M]<sup>+</sup>, 595 (19) [M-CH<sub>3</sub>]<sup>+</sup>, 443 (11) [M-C<sub>6</sub>F<sub>5</sub>H]<sup>+</sup>, 305 (7) [M]<sup>2+</sup>; HRMS (EI, 120 °C): *m/z* calcd for C<sub>34</sub>H<sub>12</sub>F<sub>10</sub>: 610.0779; found: 610.0765.

**Monochlorocorannulene (**16**):** Corannulene (**1**; 18.0 mg, 0.07 mmol, 1.0 equiv), *N*-chlorosuccinimide (9.6 mg, 0.07 mmol, 1.0 equiv) and gold(III) chloride (3.0 mol%) were dissolved in 1,2-dichloroethane (1 mL). The mixture immediately turned dark green. After stirring for 24 h at 60 °C, the mixture was diluted with dichloromethane (10 mL) and silica gel was added. The solvent was removed under reduced pressure and the crude product purified by flash column chromatography (*n*-pentane/ethyl acetate 20/1) to yield **16** together with unconverted **1** as an amorphous powder. Chromatography on silica gel with cyclohexane gave **7** as pale yellow needles (18.4 mg). Yield: 90%; m.p. 191 °C; <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>): δ = 7.72 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.7 Hz, 1H), 7.78–7.82 (m, 4H), 7.82 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.7 Hz, 1H), 7.84 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.7 Hz, 1H), 7.88 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.7 Hz, 1H), 8.01 (d, 1/2 AB, <sup>3</sup>J(H,H) = 8.7 Hz, 1H); <sup>13</sup>C NMR (175 MHz, CDCl<sub>3</sub>): δ = 136.02 (s, 1C; C<sub>hub</sub>), 135.89

(s, 1C; C<sub>hub</sub>), 135.70 (s, 1C; C<sub>hub</sub>), 135.05 (s, 1C; C<sub>hub</sub>), 134.93 (s, 1C; C<sub>hub</sub>), 131.90 (s, 1C; C<sub>flank</sub>), 131.52 (s, 1C; C<sub>flank</sub>), 131.09 (s, 1C; C<sub>flank</sub>), 131.05 (s, 1C; C<sub>flank</sub>), 130.79 (s, 1C; C<sub>flank</sub>), 128.85 (s, 1C; C<sub>cl</sub>), 127.93 (s, 1C; C<sub>rim</sub>), 127.74 (br s, C<sub>rim</sub>; 2C), 127.23 (s, 1C; C<sub>rim</sub>), 127.19 (s, 1C; C<sub>rim</sub>), 127.04 (s, 1C; C<sub>rim</sub>), 126.22 (s, 1C; C<sub>rim</sub>), 126.03 (s, 1C; C<sub>rim</sub>), 124.74 (s, 1C; C<sub>rim</sub>); IR: ν̄ = 2920 (m), 2850 (m), 1615 (w), 1298 (w), 1070 (m), 1030 (m), 861 (m), 824 (s), 782 (s), 559 cm<sup>-1</sup> (s); MS (EI, 90 °C): *m/z* (%): 248 (100) [M]<sup>+</sup>, 248 (30) [M-HCl]<sup>+</sup>, 124 (12) [M-HCl]<sup>2+</sup>; HRMS (EI, 90 °C): *m/z* calcd for C<sub>20</sub>H<sub>9</sub>Cl: 284.0393; found: 284.0395.

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