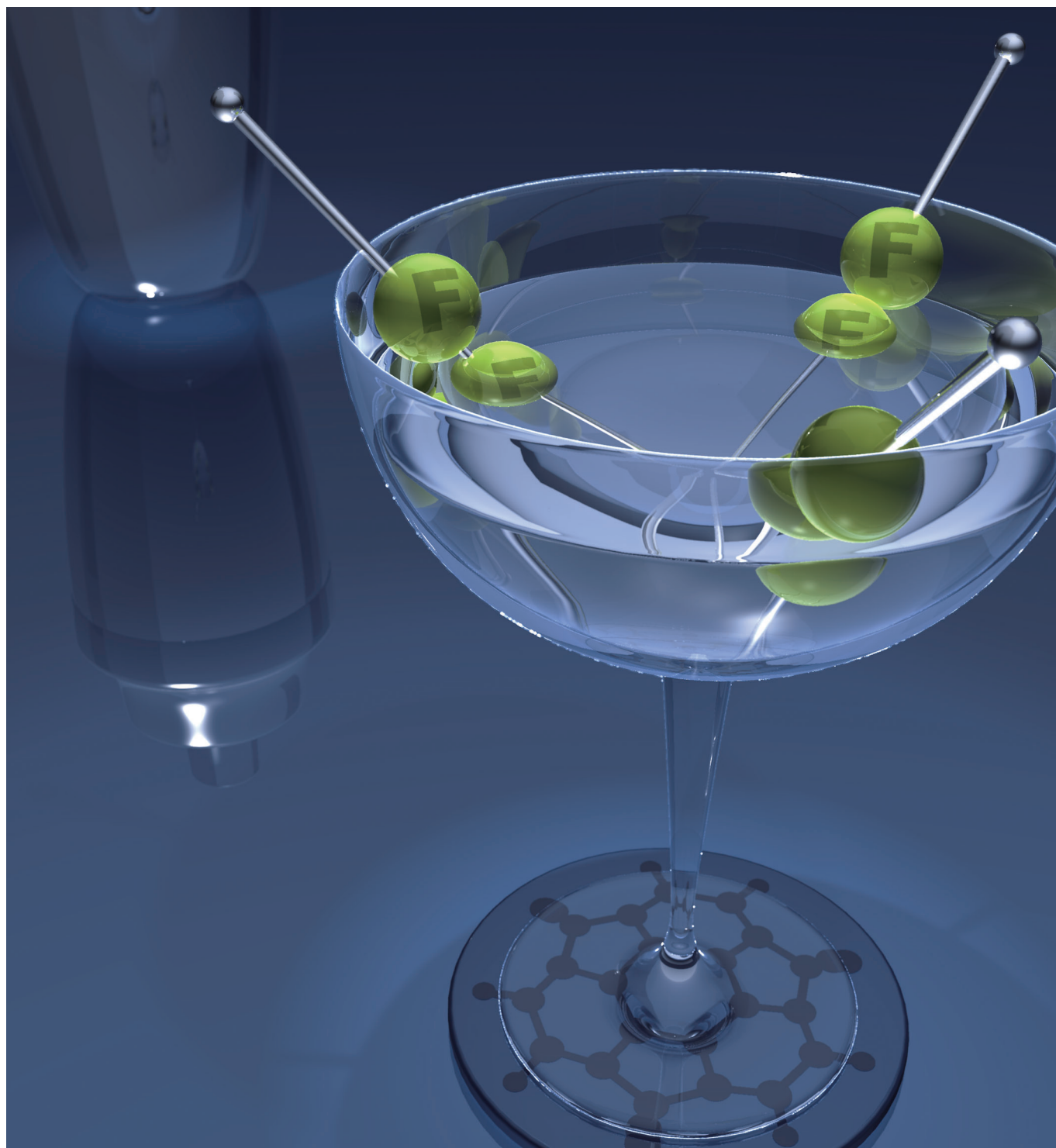


The Synthesis of Hexafluorosumanene and Its Congeners

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In crystal engineering, control of the resulting crystal-packing structure through the introduction of functional groups is important for the modification of physical properties, because substituents can initialise or inhibit the formation of the desired packing structure.

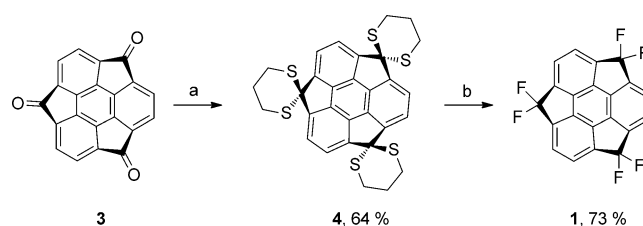
Our group^[1], amongst others^[2], were able to prove that the solid-state packing of corannulene can be tailored to give a highly ordered columnar structure. Upon introduction of two trifluoromethyl groups, the dense convex-concave π stacking of the molecular bowls of the resulting 1,2-bis(trifluoromethyl)corannulene produces a highly electric conductive material ($0.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a polycrystalline sample), with high charge carrier mobility along the intermolecular stacks.^[3] A single crystal of sumanene also exhibited high electron mobility ($0.75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) with large anisotropy determined by time-resolved microwave conductivity methods (TRMC).^[4] Not only electric conductivity is influenced by the crystal structure of the buckybowls; electroluminescence properties are also strongly dependent on their solid-state structure.^[5] Nanocrystalline assemblies of sumanenes show energy-transfer phenomena and amplified emission, when core-shell aggregates are formed.^[6]

The introduction of strong electron-withdrawing fluorine atoms to a compound or material changes the behaviour drastically and is therefore often applied in material science and physical organic chemistry. Although several substituted sumanenes have been reported,^[4b,7] not a single directly fluorinated buckybowl is known within the literature.

Here we present the first fluorinated buckybowl, hexafluorosumanene (**1**), in which all six fluorine atoms are introduced at the benzylic position in two simple steps. The introduction of fluorine atoms led to significantly lower reduction potentials and maintained an almost identical crystal packing structure to sumanene (**2**).^[7f,8]

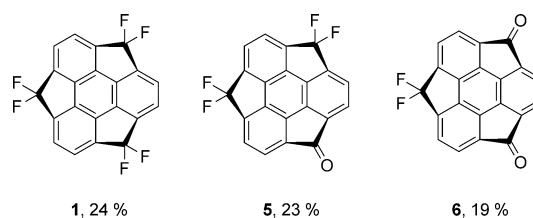
In contrast to corannulene, sumanene (**2**) offers three benzylic carbons, which can be oxidised, yielding sumanene-trione (**3**), a key compound for further transformations.^[6,9] We opted for the transformation to the cyclic dithiane **4**, because dithianes are excellent precursors for the introduction of fluorine. They are readily fluorinated by (difluoroiodo)-benzene derivatives,^[10] a combination of an electrophilic hal-

ogen and a fluoride ion donor,^[11] or even by elemental fluorine.^[12] In our case, however, early attempts using *para*-iodotoluene difluoride led to a low conversion and therefore conditions based on those reported by Katzenellenbogen^[11a] and Haufe^[11c] were tested. Using *N*-iodosuccinimide for the activation and the nucleophilic fluorinating agent pyridine hydrofluoride (Olah's Reagent) was suitable to give the desired *gem*-dihalo compound **1** in good yield (Scheme 1).



Scheme 1. Synthesis of hexafluorosumanene **1**. Conditions: a) 2900 mol % 1,3-propanedithiol, 4600 mol % boron trifluoride etherate, CH_2Cl_2 , 25 °C, 14 h; b) 2900 mol % *N*-iodosuccinimide, 34100 mol % pyridine hydrofluoride, CH_2Cl_2 , -30 °C; the reaction was carried out in a polypropylene tube.

If the reaction is carried out in a glass flask instead of a polypropylene tube, **1** is obtained in 24% yield in addition to tetrafluorosumanenone (**5**; 23%) and difluorosumanenedione (**6**; 19%) through nucleophilic attack by the liberated water. In particular, **6** is the first example of a sumanenedione derivative (Scheme 2).



Scheme 2. The mixture of products obtained if water is liberated during the reaction. Yields refer to isolated products.

NMR spectra of **1** are simple due to the C_3 symmetry. Only one signal ($\delta = 7.28$) is observed in the ^1H NMR spectrum for all equivalent rim-protons. An AB pattern ($^2J = 273 \text{ Hz}$) corresponding to three *endo*- and three *exo*-benzylic fluorine atoms is observed in the ^{19}F NMR spectrum, the chemical shift values of the doublets deviate by about $\Delta\delta = 25 \text{ ppm}$ due to ring current effects (the *exo*-fluorine atoms bear significantly more charge, than the *endo*-fluorine atoms). Likewise, the ^{13}C NMR spectrum shows only four signals with fluorine coupling constants of 261, 28 and 8 Hz (benzylic, flank and hub carbon atoms) depending on the distance to the fluorine atoms, the signal for the six rim carbon atoms is broadened.

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The redox properties of the new fluorous sumanenes were studied by cyclic voltammetry and square-wave voltammetry in THF solutions. The fluorine substitution was shown to have a drastic effect on the first reduction of the sumanene bowl. Upon introduction of six fluorine atoms, the redox potential of **1** remains irreversible, but is shifted to -1.79 V (relative to -3.21 V for **2**). An even stronger effect can be observed for the mono-one **5** and the dione **6**. Both undergo a reversible reduction in THF solution at -1.36 and -1.13 V, respectively, which is expected to take place at the carbonyl group. Hence, the irreversible reduction of **1** to the radical anion should be accompanied by immediate loss of a fluorine atom (Table 1).

Table 1. Electrochemical properties.

Compound	E° vs. ferrocene [V] ^[a]
1	-1.79 ^[b]
2	-3.21 ^[b]
3	-0.94
5	-1.36
6	-1.13

[a] The potentials are referenced to the ferrocene/ferrocinium (Fc^0/Fc^+) couple, used as an internal standard, and uncorrected for ohmic drop. Measurements were conducted in dry and degassed THF with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as conducting salt. [b] An irreversible reduction occurs in THF.

Crystals suitable for single-crystal X-ray analysis were grown by slow evaporation of a $\text{CHCl}_3/\text{EtOH}$ mixture at room temperature. A thin needle-like crystal was measured using synchrotron radiation.^[13] The molecular structure of **1** is shown in Figure 1. Substitution with bulky substituents usually results in a shallower bowl depth.^[1a,14] Surprisingly, the molecular bowl of **1** significantly deepens to $1.240(12)$ Å relative to $1.115(2)$ Å for **2**, upon introduction of the six fluorine atoms.

DFT calculations (B3LYP/6-311+G(d,p))^[17] also indicate that the bowl depth of **1** (1.22 Å) is deeper than that of **2** (1.14 Å) and trione **3** (1.19 Å), which is the deepest value among substituted sumanenes currently reported. The bowl depths of **5** and **6** are calculated to be 1.21 and 1.20 Å, respectively (ca. 0.01 Å shallower; see Table S2 in the Supporting Information).

In the experimental solid-state structure of **1**, a minor bond-length alternation is observed; the flank bond (1.389 Å) is shortened by approximately 0.011 Å, in comparison with that in **2** (1.400 Å; Table 2).

The slightly underestimated bowl depth by gas-phase DFT calculations (1.22 vs. 1.24 Å) suggests that repulsive interactions exist in the solid state, which further governs the deepening of the molecular bowl. A possible explanation might be the unfavorable interaction of the lone pairs of the *exo*-fluorine atom with the π system, which shows a pronounced shift of electron density to the exterior surface of the bowl.^[8] The repulsion would accordingly contract the bowl further.

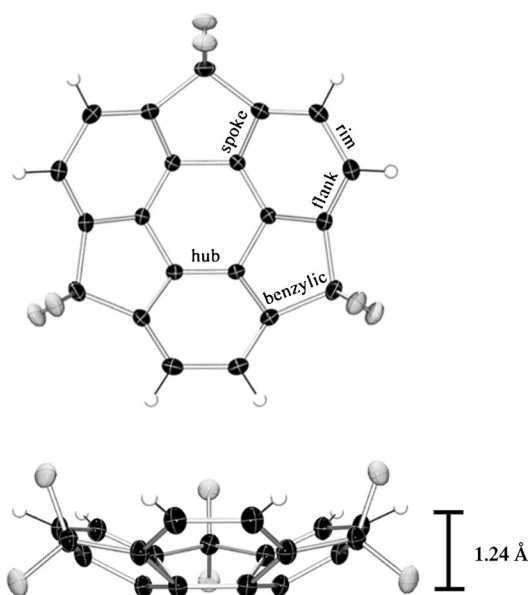


Figure 1. ORTEP^[15] representations of **1**, rendered with POV-Ray.^[16] The molecular structure of **1** in the solid state, ellipsoids drawn at the 50% probability level. Bowl depth is defined as the distance between the planes formed by the central hub atoms and the rim carbon atoms. Because of the three independent molecules in the asymmetric unit, the mean values are discussed.

Table 2. Calculated and experimental bond lengths in [Å] of **1** relative to sumanene (**2**).

Bond	$\mathbf{1}_{\text{calcd}}$ ^[a]	$\mathbf{1}_{\text{exptl}}$ ^[b]	$\mathbf{2}_{\text{exptl}}$ ^[c]
rim	1.431	1.433	1.431
flank	1.390	1.389	1.400
spoke	1.397	1.396	1.396
benzylic	1.553	1.553	1.548
hub _{short}	1.380	1.377	1.383
hub _{long}	1.439	1.440	1.429

[a] DFT calculation (B3LYP/6-311+G(d,p)). [b] Average values of all three molecules in the asymmetric unit. [c] From a previously published high-resolution X-ray dataset.^[8]

Hexafluorosumanene (**1**) shows a highly ordered columnar structure formed by concave-to-convex π - π interactions with all 1D columns oriented in the same direction, which surprisingly resembles the favourable packing of sumanene (**2**). The central six-membered rings are fully eclipsed and no slippage of the bowls can be observed, the π bowls stack perfectly over one another, therefore no transverse shifting occurs. The rim of **1** is rotated by 56° to minimise the steric repulsion of the protruding fluorine atoms, which is identical to the angle found in the solid-state structure of **2**.^[7f] Short intercolumnar C-H \cdots F interactions of 2.5 Å additionally govern the arrangement of bowls along the columnar stacks, whereas intracolumnar C-H \cdots F interactions exhibit (elongated) distances of around 2.77 Å^[18] (see Figure 2). In pristine sumanene, the *endo*-H of one sumanene interacts with the electron-rich six-membered rings of the sumanene molecule above it (distance of 2.80 Å for the short C-H \cdots π contact, comparable to contacts found for fullerenes).^[4b,19] In **1**,

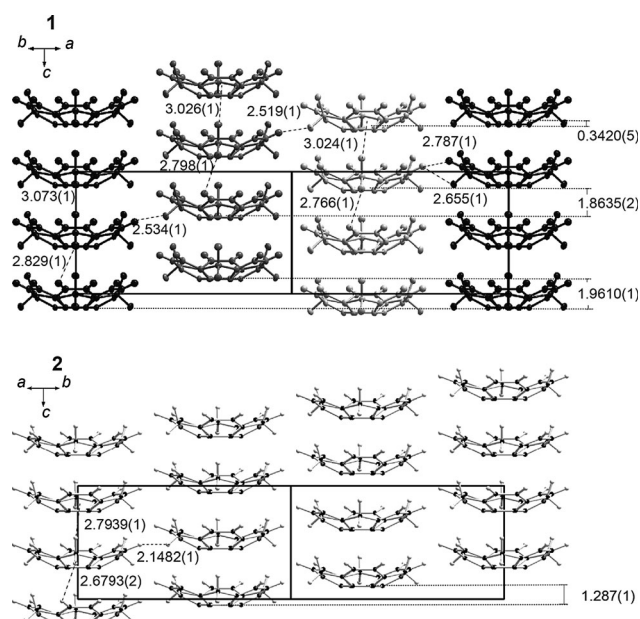


Figure 2. Representations (ellipsoids drawn at the 50% probability level) of the crystal packing in **1** (upper excerpt) and **2** (lower excerpt). Illustration of the dense arrangement of the molecular bowls which proceeds in infinite columns along the crystallographic *c* axis. For **1**, all combinations of the three crystallographically independent molecules are shown and indicated by colour (light, medium and dark grey). See the Supporting Information for additional colour representations.

the contact is slightly extended to 3.03 Å, and an overall intermolecular distance of 4.16 Å (3.86 Å for sumanene) can be observed between two stacked bowls. This increased distance is also reflected by an increase of the estimated volume per carbon atom^[2c] from 14.3 (**2**) to 16.7 Å³ (**1**). Overall, the introduction of the fluorine atoms does not significantly change the columnar packing motif, although exchanging hydrogen for fluorine atoms causes different interactions in the crystals of **1** and **2**. The crystal packing of **1** makes this system highly promising for tailor-made molecular electronics as well as the low reduction potential, concomitant with electron-acceptor abilities.

In summary, we have synthesised the first directly fluorinated bucky bowl compound and revealed the columnar-packing structure as well as low reduction potentials for all members of the family. The very electron-deficient molecule **1** is not only the deepest sumanene derivative, but also a highly promising candidate for n-type semiconductor applications, due to the efficient shielding of the molecular columns by the fluorine atoms. These results are of great interest with regard to crystal engineering, because the favourable columnar structure is completely maintained, although six functional groups are induced.

Experimental Section

Detailed synthetic procedures, electrochemical data (cyclic voltammetry and square-wave measurements) additional X-ray crystallographic de-

tails, computational details and additional data for all new compounds (NMR, MS) can be found in the Supporting Information.

Acknowledgements

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Keywords: buckybowls • crystal engineering • fluorine • pi interactions • sumanene

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- [13] CCDC-909608 (**1**) contains 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; crystal data for **1**: C₂₁H₆F₆, crystal size 0.16 × 0.08 × 0.06 mm; *M_r* = 372.26; trigonal; space group *P3c1*; *a* = 17.064(1), *b* = 17.064(1), *c* = 8.333(1) Å; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; *V* = 2101.3(3) Å³, *T* = 100(2) K, *Z* = 6, synchrotron radiation ($\lambda = 0.69000$ Å), $\mu = 0.146$ mm⁻¹, 43736 reflections measured, 4447 independent reflections (*R*_{int} = 0.0567). The final *R*₁ values were 0.0457 [*I* > 2σ(*I*)] and 0.0544 (all data). The final *wR*(*F*²) values were 0.1134 [*I* > 2σ(*I*)] and 0.1187 (all data). The goodness of fit on *F*² was 0.986.
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