

Highlight Review

Syntheses and Properties of Buckybowls Bearing Electron-withdrawing Groups

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Abstract

This review provides an overview on recent advances in the novel field of electron-poor buckybowls. Whereas buckybowl chemistry has now been studied for more than two decades, only recent developments have drawn attention to this type of compound. The syntheses of these buckybowls and their distinct and characteristic properties are described.

Introduction

Due to their appealing and unique properties, carbon-rich compounds such as fullerenes (buckyballs), carbon nanotubes (buckytubes), and graphene have been the subject of intense research for decades. Their outstanding and superior characteristics render them ideal candidates for the application in molecular electronics, material sciences, and nanotechnologies.

Bowl-shaped polycyclic aromatic hydrocarbons (buckybowls, Figure 1) can be considered as substructures of fullerenes with three-dimensional bowl shape or as the polar end caps of carbon nanotubes but yet they differ remarkably in their physicochemical properties.

Several accounts have been published in the past years such as the review of Siegel and co-workers, dealing with structures and physical properties of bowl-shaped hydrocarbons¹ and the review of Scott and co-workers, with its focus on nonplanar polycyclic aromatic hydrocarbons synthesized by flash vacuum pyrolysis.² A more specialized review was published in 2011 covering recent developments and gives a detailed overview regarding the synthesis and properties of molecular clips and tweezers, derived from corannulene (**1**).³ A brief review from 2013 summarizes recent advances in the synthesis of novel bowl-shaped compounds and explains topologically distinct approaches for the synthesis of molecular bowls (“fold-in” vs. “stitching”).⁴ The buckybowl sumanene (**2**) was the subject of recent review articles as well, Sakurai and Higashibayashi⁵ and Amaya et al.⁶ published reviews concerning the synthesis of sumanenes and related buckybowls. Additionally the book “Fragments of

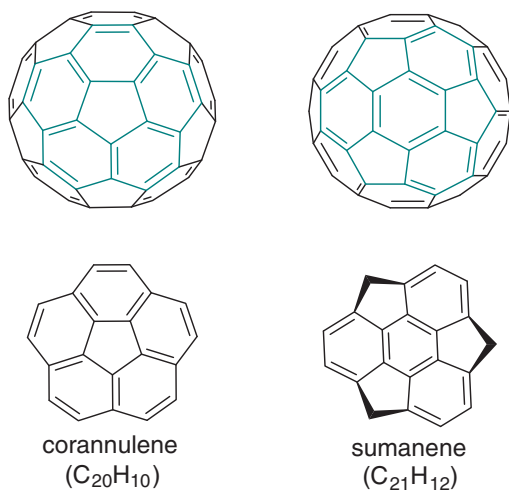


Figure 1. Corannulene (**1**) (left) and sumanene (**2**) (right) are fullerene substructures.

Fullerenes and Carbon Nanotubes” was published, where several of the aforementioned groups as well as other groups contributed on the syntheses, reactions, and coordination chemistry of fullerene fragments and carbon nanotubes (CNTs).⁷

In this review, the syntheses of buckybowls bearing electron-withdrawing groups introduced by liquid-phase synthesis and by means of gas-phase reactions will be presented. The final chapter will describe computational efforts to investigate such compounds. The focus was placed on the electronic properties of these compounds and their solid-state assemblies.

Functionalized Buckybowls by Liquid-phase Synthesis

Several brominated and chlorinated corannulenes **3–8** (Figure 2) were amongst the first synthesized electron-deficient buckybowls and were used as starting material for further derivatizations and will not be discussed in detail.⁸

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 applications such as liquid crystals, dyes, surfactants, conductive polymers, pharmaceuticals, and agrochemicals.⁹ Fluorinated polycyclic aromatic hydrocarbons and novel buckybowls by C–F activation.¹⁰ Our group started the investigation on electron-poor buckybowls in 2009, focusing on fluorination and trifluoromethylation.

Schmidt et al. synthesized corannulenes bearing fluorine-, trifluoromethyl-, and pentafluorophenyl groups **9**, **10**, and **15–20** (Scheme 1) by starting from corannulene **1** and by employing a

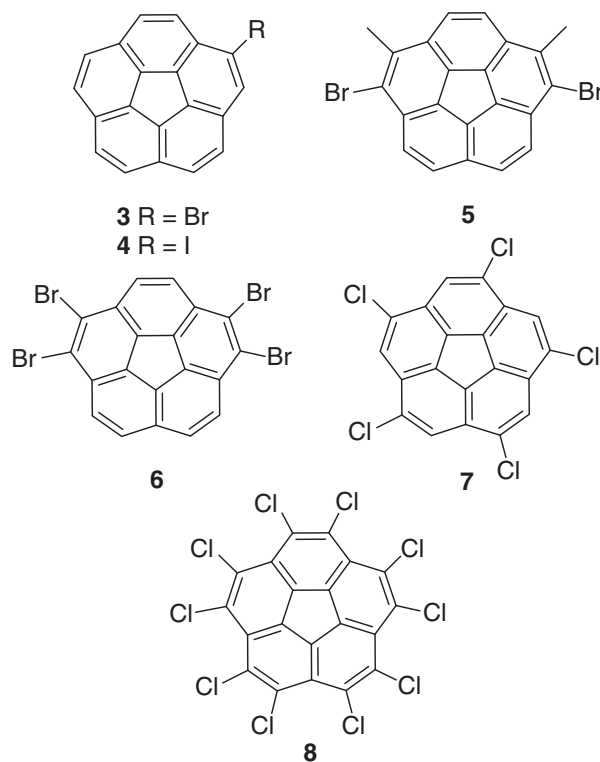
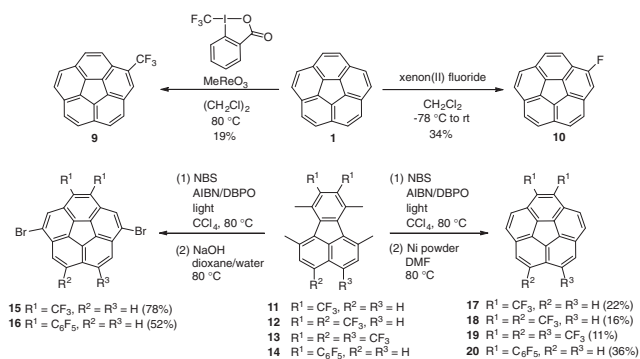


Figure 2. Commonly used corannulene building blocks **3–8**, not comprehensive.⁸



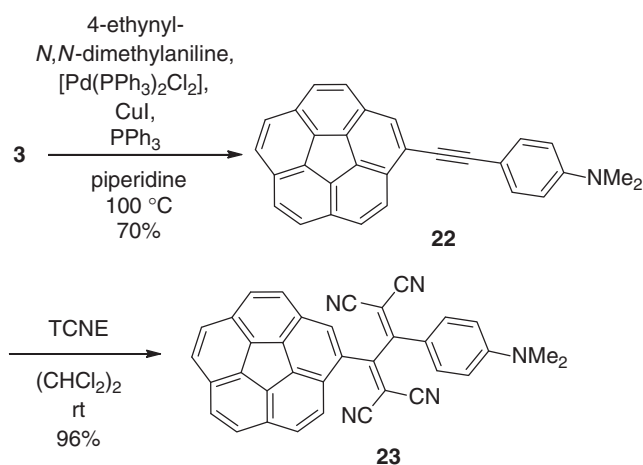
Scheme 1. Corannulenes bearing F, CF₃, and C₆F₅ groups.¹¹

strategy to construct suitable fluoranthenes **11–14** according to an early synthesis described by Siegel and co-workers.¹² These fluoranthene precursors are generated from an activated alkyne bearing two electron-withdrawing groups and a diene. Depending on two different reaction conditions, this method allows the systematic synthesis of brominated **15** and **16** or non-brominated corannulenes thereof **17–20** (Scheme 1).^{12b}

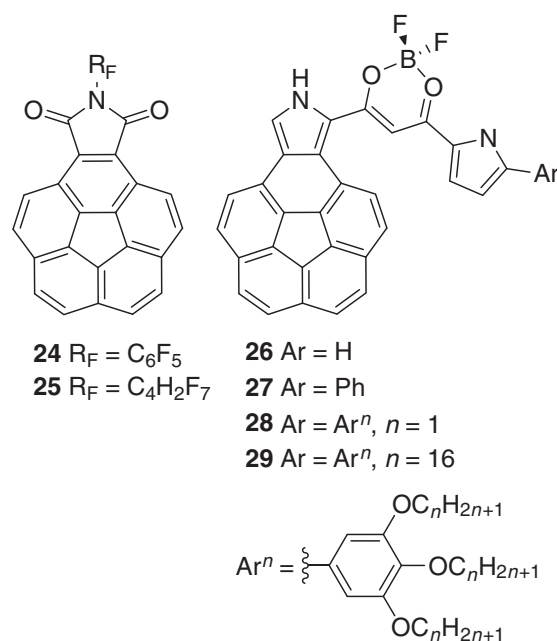
Single-crystal X-ray analyses revealed a very regular columnar π -stacking of both (bis)trifluoromethylated corannulenes **15**^{11a} and **17**.^{11b} A monofluorinated **10** prepared from **1** and xenon difluoride and a monochlorinated corannulene **21** were reported and crystallized as well. Both compounds show only a slipped stacking motif.^{11a}

Because of the highly regular and densely packed π -stacking structure,^{11b} the charge-carrier mobility of trifluoromethylated corannulene **17** was investigated together with the parent corannulene **1** (for comparison). A charge-carrier mobility of 0.9 cm² V⁻¹ s⁻¹ was observed for **17**,^{11b} even surpassing the charge-carrier mobility of sumanene **2** (0.75 cm² V⁻¹ s⁻¹).¹³ The noncolumnar order in solid-state pristine corannulene leads to a much lower value of less than 5 × 10⁻⁴ cm² V⁻¹ s⁻¹. Additionally, electrochemical investigations showed that the electron-acceptor strength follows the general order CF₃ > C₆F₅ > Cl > F and is highly dependent on the position of the substituent on the corannulene rim.^{8c}

Electron-deficient corannulenes bearing one, two, and five cyanobutadienyl groups were investigated, by using the aforementioned halogenated corannulenes **3**, **5**, and **7**, following the reaction conditions used by Wu et al. for their comprehensive study on multiethynylcorannulenes.^{8h} Both groups of corannulenes bearing electron-donating substituents (exemplarily shown with one substituent in Scheme 2, compound **22** obtained from brominated corannulene **3**) and the group of corannulenes bearing electron-withdrawing substituents (exemplarily shown again in Scheme 2, **23** obtained from electron-rich **22**) were studied in regards to their optical and electronic properties. Again, the exact position of the substituents, the molecular symmetry and the stability of oxidized, reduced, or excited states make critical contribution to their overall properties.¹⁴ Thus, no simple correlation with the number of substituents can be observed.^{8c,11a} The compounds, however, show fascinating properties such as fluorescence, multiple reduction states, and intramolecular charge-transfer. The reduction potential is shifted by roughly 1.64 V for the compound derived from **5** (thus bearing two of the cyanobutadiene motifs shown in Scheme 2)



Scheme 2. The reaction pathway leading to push–pull corannulenes as synthesized by Wu et al.¹⁴



Scheme 3. A similar corannulene with R = H was also prepared but not characterized, see ref 12b.

and **7** (symmetrically bearing five cyanobutadiene motifs) compared to pristine corannulene **1**, making them by far the strongest electron-accepting corannulenes.¹⁵

Two groups of π -extended corannulenes, substituted pyrrole-fused corannulenes **26–29** and imide-fused perfluoroalkylated corannulenes **24** and **25** were published by Bando et al.¹⁶ and Schmidt et al.,¹⁷ respectively (Scheme 3). Although their structures are only remotely similar, both groups show a favorable self-assembly in the solid state. The imide-fused corannulenes **24** and **25** are strong electron-acceptor molecules in solution, show a nearly perfect close π -stacking in a convex–concave fashion (Figure 3), and are expected to possess useful electronic properties,¹⁷ likewise to the aforementioned charge-carrier mobility of the trifluoromethylated corannulene **17**^{11b} and pristine sumanene (**2**).¹³ The π -conjugated anion-receptor cor-

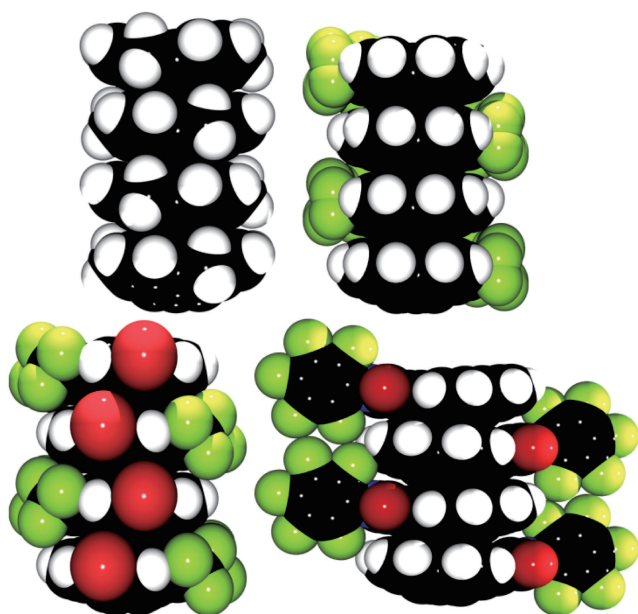


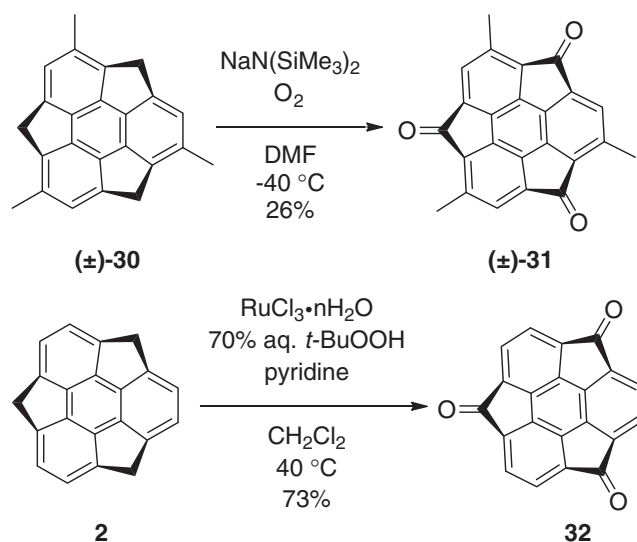
Figure 3. Excerpts of the favorable solid state packing of **2** (top left), **17** (top right), **15** (bottom left) and **24** (bottom right).

annulenes **26–29** were found to exhibit liquid-crystalline behaviors and showed intrinsically higher charge-carrier mobilities of up to $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, extended π -conjugation and anion binding.¹⁶

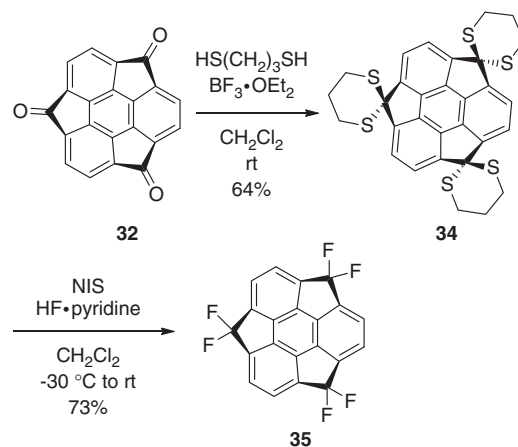
In 2003, the group of Sakurai succeeded in synthesizing the molecular bowl sumanene (**2**) ($\text{C}_{21}\text{H}_{12}$),¹⁸ which can also be considered as a curved subunit of the fullerene C_{60} (Figure 1). The stability of sumanene (**2**) was predicted several years before,¹⁹ but attempts to synthesize it, failed.²⁰ At last, the key to success was to construct a 3D framework mostly based on tetrahedral sp^3 carbons. The π -conjugated bowl was finally obtained by oxidative aromatization.

The first synthesis of a sumanenetrione was reported in 2010. A low-temperature reaction in the presence of molecular oxygen and sodium bis(trimethylsilyl)amide was used to oxidize racemic trimethylsumanene **30** to the corresponding trimethylsumanenetrione **31** (Scheme 4).²¹

The deeper bowl of the compounds results in a higher bowl inversion energy barrier than pristine sumanene (**2**)²³ and enabled Tsuruoka et al. to resolve (\pm)-**31** by the use of a chiral HPLC column. The enantioenriched **31** was used to quantify the bowl inversion energy barrier of **31** by CD spectra measurements (23.4 and $23.3 \text{ kcal mol}^{-1}$ in acetonitrile and dichloromethane, respectively). One year later in 2011, Amaya et al. developed a convenient access to trione **32** and succeeded in synthesizing monoxidized sumanenone **33** in good yields as well.²² The compounds were thoroughly characterized and investigated electrochemically. Extremely strong anodic shifts are observed for the first reduction potentials of both compounds, the direct comparison to sumanene (**2**) reveals a shift of 2.08 V for trione **32** and a shift of 1.26 V for **33**. The monooxosumanene **33** was also studied crystallographically and found to exhibit close ($3.82\text{--}3.87 \text{ \AA}$) columnar stacking in the solid state, comparable to the favorable structure of sumanene (**2**) itself. An extensive computational study was published in



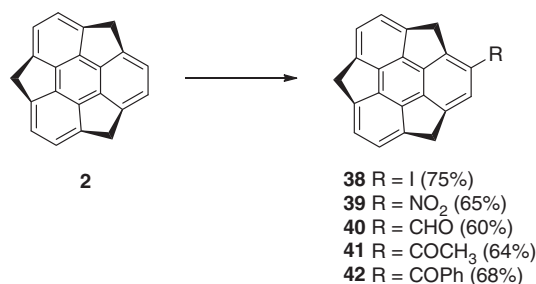
Scheme 4. Preparations of sumanenetriones **31** and **32**.^{21,22}



Scheme 5. The synthesis of hexafluorosumanene **35**.²⁶

2012 investigating the structures and spectroscopic properties of sumanene (**2**) and the two known oxosumanenes **32** and **33**.²⁴ Morita et al. utilized the unique properties of trione **32** to form *onigiri*-type organic–organic core–shell assemblies consisting of nanocrystals of sumanene (**2**) as the shell and trione **32** as the core, which show an amplified emission attributable to an energy-transfer phenomenon.²⁵

The cyclic dithiane **34** can be easily prepared from trione **32**. Compound **34** is an excellent precursor molecule for the introduction of fluorine. In the presence of excess pyridinium poly(hydrogen fluoride) and *N*-iodosuccinimide in a polypropylene tube, hexafluorosumanene **35** is obtained in good yields (Scheme 5). However, if the reaction was carried out in a glass flask, **35** is obtained in only 24% yield in addition to tetrafluorosumanenone **36** (23%) and difluorosumanenedione **37** (19%), because water is liberated from the glass surface of the flask due to the presence of hydrogen fluoride. All fluorinated compounds were studied electrochemically and show diverse reduction potentials. The solid-state X-ray structure analysis of **35** revealed two surprising features. The bowl is



Scheme 6. Aromatic electrophilic substitution reactions of sumanene (**2**).²⁷

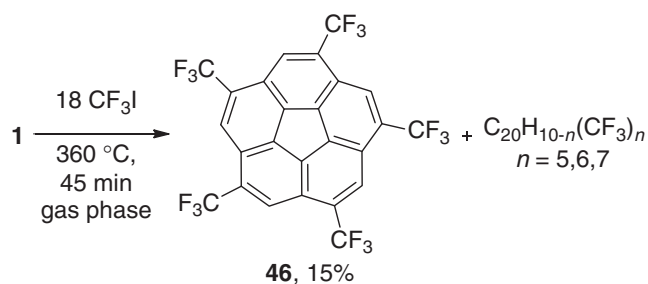
significantly deepened upon the introduction of the six fluorine atoms (1.24 Å) and the columnar solid-state packing is retained, although the intermolecular π - π -stacking distance is slightly elongated. DFT calculations support the obtained data.²⁶

Electrophilic substitution reactions of sumanene (**2**) were studied and mono-, di-, and trisubstituted sumanenes were prepared (exemplarily depicted for the synthesis of monosubstituted sumanenes **38–42** in Scheme 6). The regioselectivity was studied additionally by DFT calculations comprehensively. The laborious separation of the disubstituted regioisomers was achieved with PTLC or HPLC techniques and all regioisomers were isolated and completely characterized. Surprisingly the X-ray crystallographic data for two compounds (2,9-diiodo-sumanene (**43**) and 2,9-diacetylsumanene (**44**)) does not show a perfect columnar solid-state stacking structure like the parent sumanene molecule. Diiodosumanene **43** adopts a structure similar to the previously reported tris(methylsulfonyl)triazasumanene **45**,²⁸ a *quasi* convex–convex and concave–concave alignment and a deepened bowl (1.18 Å), **44** on the other hand shows a slipped stacking packing where neighboring columns are facing opposite directions.²⁷

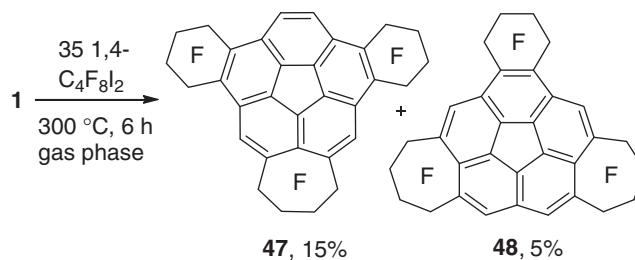
Functionalized Buckybowls by Gas-phase Reactions

After the discovery of fullerenes, heterogeneous gas-phase reactions were commonly used for their derivatization. This type of reaction, however, has several major drawbacks, such as low selectivity, low tolerance of functional groups due to radical mechanisms, and high temperatures above 300 °C. This narrows the application of this method to only a few substrates which tolerate the described reaction conditions. The purification of the resulting reaction mixtures is almost exclusively required to be done by (multistage) HPLC purification. Nevertheless, novel electron-deficient corannulenes were prepared by this method.

In 2012 Kuvychko et al. reported the heterogeneous gas-phase trifluoromethylation of corannulene (**1**) with excess trifluoromethyl iodide (Scheme 7). Although several compounds were visible in the mass spectrum and HPLC trace of the crude reaction mixture, only one compound, the symmetric 1,3,5,7,9-pentakis(trifluoromethyl)corannulene (**46**), was isolated successfully after HPLC separation. The compound was studied by single-crystal X-ray analysis and an almost perfect columnar π -stacking was observed. The molecular bowl is flattened to 0.788(15) Å and alternate stacks face opposite directions, with an intermolecular π - π stacking distance of approximately 3.8 Å.



Scheme 7. Gas-phase trifluoromethylation of corannulene (**1**).²⁹



Scheme 8. Gas-phase annulation of corannulene.¹⁵

Besides the regular solid-state alignment, another remarkable property is again the unexpected strong electron affinity of trifluoromethylated **46**, being shifted by almost 1 V in comparison to the parent corannulene (**1**), obtained from electrochemical measurements in solution.²⁹

By applying similar reaction conditions, Kuvychko et al. reported a high-temperature reaction of 1,4-C₄F₈I₂ with corannulene (**1**). Again, a mixture of various products was obtained as indicated by mass spectrometry and NMR analysis. One major product and one side-product were isolated from the crude mixture in 15 and 5% yield, respectively, where six H atoms are substituted by three C₄F₈ moieties that form six- and seven-membered rings (Scheme 8). The annulated compound **47** was studied crystallographically but does not show the desired columnar π - π interactions. Its bowl-depth is lowered to 0.783(48) Å, most likely to avoid steric strain at the rim. The gas-phase electron affinity of **47** and its reduction potential in solution were measured to quantify the effect of the annulation on the corannulene molecule. The direct measurement of the electron affinity resulted in a value of 2.74 ± 0.02 eV, which makes the corannulene **47** an even stronger electron acceptor than the fullerene C₆₀ (2.689 ± 0.008 eV),³⁰ which is already used in various donor–acceptor arrays for the design of artificial photosynthetic systems with efficient and long-lived charge separation. In solution, the reduction potential is shifted by 1.23 V vs. pristine corannulene (**1**) as a result of the stronger electron-withdrawing ability of the C₄F₈ rings and the substitution pattern in **47**. Surprisingly, the fullerene C₆₀ remains a stronger electron acceptor in solution, which the authors proposed is caused by differences in the solvation energies.¹⁵

Computational Studies on Electron-deficient Buckybowls

Theoretical predictions become more and more accurate

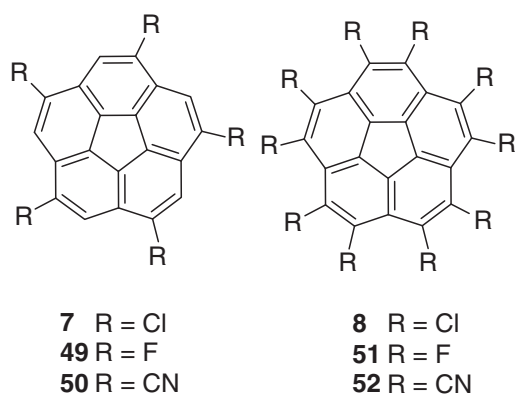


Figure 4. Corannulenes **7**, **8**, **49**, and **50** bearing electron-withdrawing groups in the described studies.

over the time and allow comparatively simple access to geometric and electronic parameters and hence properties of molecules, that are currently synthetically inaccessible. Several studies dealing with electron transport and optical properties were for example recently published by Zoppi et al.³¹

García-Novo et al. studied corannulenes **7**, **8**, and **49–52** bearing five or ten F, Cl, or CN groups by means of density functional theory and MP2 methods (Figure 4). For the compounds **7**, **49**, and **50**, the geometry of the corannulene bowl remains almost unaffected. Only a slight flattening of the bowls is observed. The shallowest bowl in this series is the pentachlorinated **7**, which most likely originates from the sterical bulk of the chlorine atoms. For the pentafluorinated corannulene **49**, almost no change was observed. When all aromatic hydrogen atoms are replaced, more dramatic changes of the geometry are observed. As expected, the most striking effect corresponds to decachlorinated **8**, where the bowl depth is reduced to 0.55 Å. Nitrile **52** is also flattened (0.73 Å), whereas for the decafluorinated corannulene **51** almost no changes (0.89 Å) are predicted.

The introduction of electron-withdrawing substituents largely affects the electrostatic potential of both the convex and the concave side of the studied compounds. For the pentasubstituted corannulenes **7**, **49**, and **50**, zero or positive potentials are found, whereas all decasubstituted derivatives **8**, **51**, and **52** show clearly positive electrostatic potentials. All studied compounds were shown to interact favorably with the anions Cl^- , Br^- , and BF_4^- via the conjugated system, preferentially on the concave side.³² Complementarily, Josa et al. studied dimers of corannulene bearing electron-withdrawing groups for fullerene recognition.³³

Dos Santos et al. investigated 13 fluorinated corannulenes (Figure 5) by density functional theory calculations. Fortunately, the calculations suggest that both $\text{C}_{20}\text{F}_{10}$ **51** and $\text{C}_{20}\text{F}_{20}$ (all peripheral rim hydrogen atoms are substituted by two F atoms) **53** are more stable than corannulene itself. The HOMO–LUMO gaps of all studied compounds are strongly dependent on the concentration and the position of the incorporated F atoms.³⁴ This supports the experimental findings of Schmidt et al.^{11a} and Kuvychko et al.¹⁵

Purushotham et al. investigated conjugated, acene-fused buckybawls (Figure 6) in regards to their suitability to use this

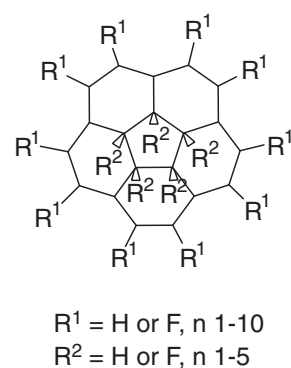


Figure 5. Hydrogenated and fluorinated corannulenes studied.³⁴

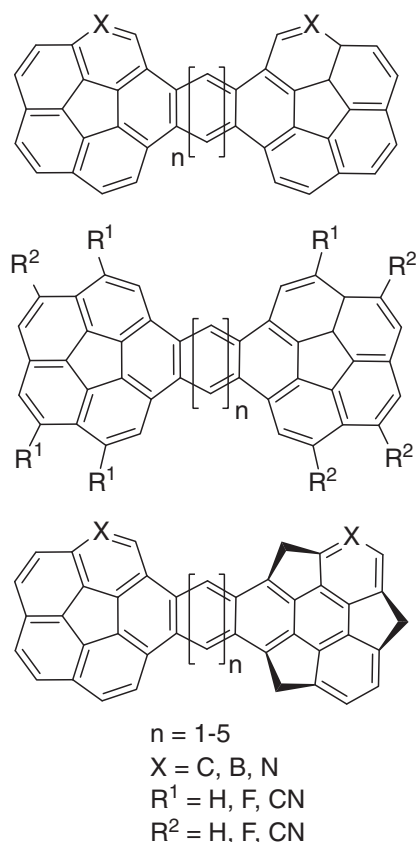


Figure 6. An excerpt of the systems considered in the study of Purushotham et al.

class of compounds for p-type, ambipolar and n-type organic semiconductors.³⁵

The studied compounds include several groups of compounds including boron- and nitrogen-doped buckybawls sumanene and corannulene bowls which are fused with a series of acenes starting from benzene up to pentacene. Additionally homo- and heterodimers and substituents were considered and calculated on a B3LYP/6-311+G(d) and B3LYP/6-31G level of theory. Their analysis reveals that some nitrile substituted, boron- or nitrogen-doped acene-fused dimers can indeed be expected to be air-stable n-type and ambipolar semiconductors.³⁵

Conclusion and Outlook

Although probably falsely claimed in 2013,¹⁵ the annulated corannulene **47** is by far not the strongest electron-accepting corannulene, the group of Diederich and Siegel published two superior acceptor molecules earlier in 2012¹⁴ and the widely used oxosumanene **32**^{22,26} also might be a stronger electron acceptor than C₆₀, even though the compounds were only investigated electrochemically in solution and not additionally by photoelectron spectroscopy in the gas phase.

The extended family of electron-deficient curved carbon-based π -systems already shows fascinating properties and makes them excellent candidates for electrochemically active functional materials and the range of properties is expanding continuously.

We thank the Deutsche Forschungsgemeinschaft (GRK 1582/1) for support of our work.

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