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Corannulenylerrocenes: towards a 1D, non-covalent metal–organic nanowire†

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A class of novel corannulene-derived ferrocene donor–acceptor systems has been synthesized by straight-forward Negishi-type coupling of iodocorannulene. Their solid state structures have been studied crystallographically and found to exhibit unique inter- and intramolecular slipped stacking interactions.

Non-covalent interactions like hydrogen bonding, π -stacking, van der Waals forces or electrostatic interactions are much weaker than covalent interactions. Still they are able to force self-assembly (*e.g.* in proteins or nucleic acids) and can be tuned to assemble a molecule into the desired form. It is essential to develop new types of molecules that show suitable properties which can be used for electronics on a molecular scale.¹ However research on molecular electronics has scarcely been investigated on bowl-shaped π -aromatic systems like corannulene (**1**).² While sumanene exhibits one-dimensional anisotropic conductivity³ and its crystal structure is characterized by columnar π -stacking,⁴ the solid state structure of **1** is dominated by H $\cdots\pi$ -interactions.⁵ Recently, a comprehensive in-depth structural analysis of crystal packing trends of polycyclic aromatic bowls has been published, showing the diversity of this system.⁶

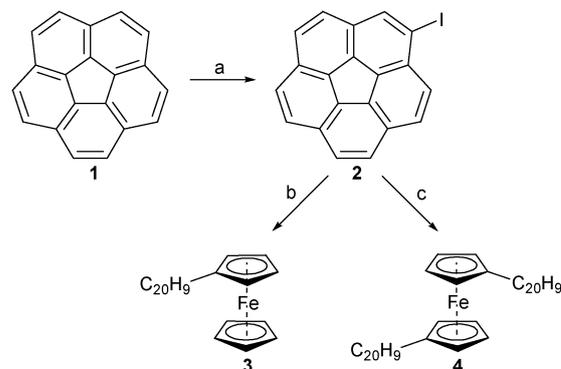
Compounds comprising two connected corannulene bowls have attracted considerable attention. The exhaustively studied bicorannulene, composed of two chiral bowls tethered by a single bond, possesses 12 chiral conformers.⁷ The formation of supramolecular complexes between larger connected systems and fullerenes has been utilized as “buckycatchers”; the published association constants, however, are rather low.⁸ Upon alkali metal reduction, corannulene is able to accept up to four electrons (in the case of lithium).⁹ A sandwich structure was proposed for the resulting anion several years ago, supported by multi-nuclear NMR spectroscopy¹⁰ and recently the

group of Petrukhina succeeded in investigating its solid state structure.¹¹ The reduction of bicorannulene leads to the formation of supramolecular oligomers,¹² while a related 1,8-dicorannulenyloctane appears to aggregate in the same way as unsubstituted **1**.¹³ Although the electro-chemistry of corannulene and some derivatives has been investigated as well, electrochemical reduction beyond the unstable trianion was not achieved in any case.¹⁴

Herein we report the use of a redox-active organometallic spacer to connect two corannulene moieties. A ferrocene scaffold allows rotation of both connecting σ -bonds but is rigid regarding the perpendicular axis. The distinctive feature of this assembly is the in-plane rotation of the cyclopentadienyl ligands which allows the system to choose its conformation freely in its particular chemical environment. Moreover, ferrocene is a suitable one-electron donor creating donor–acceptor systems when connected to one or more annulene fragments.

We first developed an efficient synthetic access to iodocorannulene (**2**), a versatile corannulene building-block for cross-coupling reaction.¹⁵ Adapting Wang’s gold(III)-catalysed halogenation protocol,¹⁶ **2** was obtained in yields of up to 99% from corannulene and *N*-iodosuccinimide.

Corannulenylerrocene (**3**) was obtained after lithiation, zincation and subsequent Negishi-type coupling of ferrocene and **2** (Scheme 1) in 42% yield after column chromatography



Scheme 1 (a) 1.0 eq. *N*-iodosuccinimide, 5.0 mol% gold(III)-chloride, 1,2-dichloroethane, 48 h rt, 3 h reflux; (b) 2.0 eq. ferrocenyl zinc chloride, 1.0 mol% palladium(II) acetate, 2.0 mol% triphenylphosphane, THF, 48 h, 60 °C; (c) 0.5 eq. 1,1'-bis(chlorozincio)ferrocene, 1.25 mol% palladium(II) acetate, 2.5 mol% triphenylphosphane, THF, 12 h, 70 °C.

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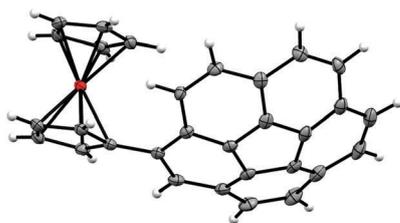


Fig. 1 Structure of **3** as represented by the asymmetric unit. Ellipsoids drawn at 50% probability.

on neutral aluminum oxide. For the synthesis of 1,1'-dicorannulenyferrocene (**4**), 1,1'-dibromoferrocene proved to be the most convenient precursor to generate 1,1'-dilithioferrocene *in situ* without the use of TMEDA. Subsequent metathesis with zinc chloride yields 1,1'-bis(chlorozincio)ferrocene, which was immediately used for Negishi-type cross-coupling. Avoiding TMEDA seems to be crucial for the cross-coupling reaction to occur,¹⁷ as no product was isolated when using 1,1'-dilithioferrocene–TMEDA complex for metathesis and subsequent cross-coupling.

The structure of **3** was determined by single-crystal X-ray diffraction (Fig. 1).[‡] Similar to the unsubstituted corannulene,⁵ it is dominated by intermolecular C–H··· π -interactions,¹⁸ in this case from a corannulene hydrogen to the convex surface of an adjacent corannulene ranging from 2.7 to 3.2 Å, as well as weak interactions from the corannulene open face bowl towards an oppositely facing C₅H₅-ring. The rim region of corannulene features a less negative electrostatic potential relative to the hub region and thus facilitates this type of interaction.¹⁹ Every molecule in the orthorhombic unit cell acts as both a donor and an acceptor of at least one C–H··· π contact. (Fig. 2). The bowl depth of this corannulene derivative (0.864(1) Å) is virtually identical to that of corannulene (0.8784(5) Å).¹⁹

Introducing a second corannulene moiety to this system changes the solid state arrangement drastically (Fig. 3 and 4).

It is best described by three striking features: intramolecular concave–convex offset π -stacking of the two corannulene bowls, close intermolecular C–H··· π contacts between the hydrogen atoms of corannulene and a six-membered ring of the bowl of another column of stacked molecules (approx. 2.83 Å to the center of the ring) and intermolecular π -stacking between the double-decker alignment of **4**. Two molecules are present in the asymmetric unit that forms π - π contacts with an identical enantiomer along the *c*-axis. The different enantiomers are

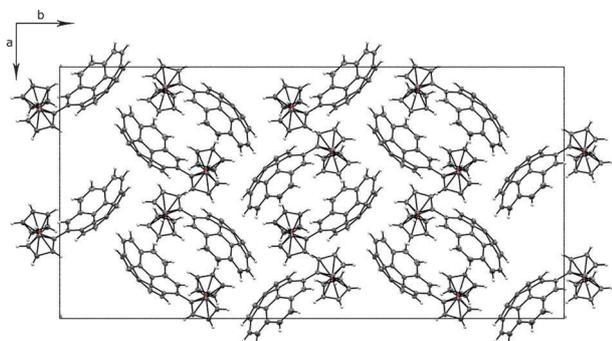


Fig. 2 Orientation of **3** in the solid state structure, view along the crystallographic *c*-axis.

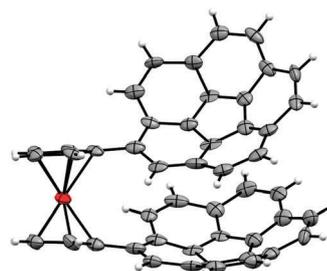


Fig. 3 Structure of **4** as represented by one half of the asymmetric unit. Ellipsoids are drawn at 50% probability. A deformation of the sandwich structure is present in both enantiomers, with a tilt angle between the iron centre and the centre of the cyclopentadienyl ring averaging to 5.5° (1.2° for **3**). Like the structure of **3**, the ferrocene has an eclipsed conformation in the solid state.

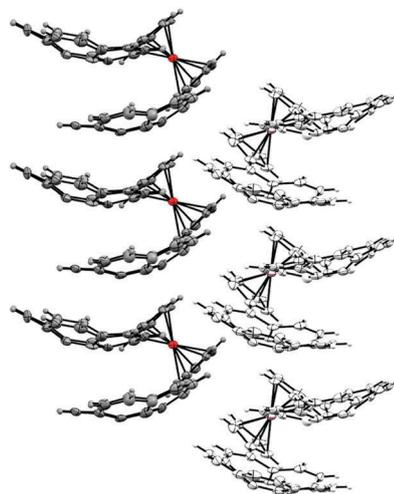


Fig. 4 Stacking motif of **4** between four molecules. View along the crystallographic *b*-axis. Molecules I: light grey, molecules II: dark grey, the Fe atoms are marked in red.

interacting *via* C–H··· π contacts with each other. In conclusion, it seems favourable to avoid perfect columnar stacking to facilitate C–H··· π contacts by tilting the bowls. Again, the small differences in the electrostatic potential of the rim gives direction to interaction with the π basicity of the central five-membered ring. Although we found a plethora of interactions between the molecular units, remaining voids of 100 Å³ on the crystallographic axis are located at 0.5 0 0 and 0 0.5 0, which are hosting a disordered solvent molecule. In contrast to other bowl-shaped molecules, neighbouring columns show identical bowl directions.²⁰

Both compounds are deep red solids. In dichloromethane absorption maxima in the UV (**3**: 251 and 294 nm; **4**: 248 and 292 nm) and a very broad band in the visible region around 425 nm can be observed.

The redox properties of **3** and **4** were preliminarily studied by cyclic voltammetry (CV; see ESI[†]). All potentials are referenced *vs.* the decamethylferrocene redox couple [Cp*₂Fe]⁰/[Cp*₂Fe]⁺, Cp* = C₅Me₅ as the internal reference to avoid overlap of the signals of the ferrocenyl group in **3** and **4** with the signal of free ferrocene. In our setup, Fc⁰/Fc⁺ was found to be at –0.56 V (dichloromethane), –0.48 V (THF) *vs.* Fc/Fc⁺.

In dichloromethane a reversible redox process for the ferrocenyl groups can be observed in the anodic CV sweep

for both molecules (**3**: 0.58 V, **4**: 0.57 V). In comparison to plain ferrocene, an electron withdrawing effect of the corannulene substituent would be expected, but the effect is very small and lies within the experimental error. For the reduction of the corannulene unit, an irreversible process in the cathodic region at about -1.87 V for **3** and -1.85 V for **4** can be observed. Since the window for measurements in this region is rather limited in dichloromethane, interpretive problems prohibit precise conclusions.

Measurements in THF were also conducted, showing a reversible process for the redox step of the ferrocene unit again close to the value of unsubstituted ferrocene. The small difference between the oxidation step of **3** (0.50 V) and the oxidation step of **4** (0.45 V) might arise from the mesomeric effect as previously described by Astruc *et al.*²¹ which stabilizes the positive charge in the ferrocene unit. THF as a Lewis basic solvent stabilizes the oxidized state of the ferrocene unit; for steric reasons this is easier to achieve for the unsubstituted ferrocene. Here, the solvent effect seems to predominate, comparing **3** to ferrocene. **4** seems to be well stabilized by the mesomeric effects resulting from two corannulene units.

Two reductions can be observed for **3** (-2.03 V and -2.51 V). The reduction waves of **4** (-2.05 V, -2.56 V) indicate that two one-electron steps take place. Since both reduction steps are well separated from each other it can be assumed that one corannulene unit undergoes two reduction steps to the dianion. THF is apparently not an appropriate environment to stabilize the negatively charged corannulenes; the reduction is shifted further to the cathodic region in comparison to dichloromethane.

In summary we have designed a new class of molecular architectures, corannulenylderocenes, starting with the synthesis of versatile iodocorannulene. The new compounds were fully characterized. Their solid state structure depends on the number of attached annulenes. While corannulenylderocene is characterized by $H \cdots \pi$ interactions, 1,1'-dicorannulenylderocene shows the desirable π -stacking motif.

Notes and references

† *Crystal data for 3*: $C_{30}H_{18}Fe$, $M = 434.29$, orthorhombic, $a = 22.011(5)$ Å, $b = 43.742(9)$ Å, $c = 8.1622(17)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 7858(3)$ Å³, $T = 133(2)$ K, space group $Fdd2$, $Z = 16$, $\mu(\text{MoK } \alpha) = 0.783$ mm⁻¹, 25 166 reflections measured, 5905 independent reflections ($R_{\text{int}} = 0.0455$). The final R_1 value was 0.0429 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.0925 ($I > 2\sigma(I)$). The final R_1 value for all data was 0.0554. The final $wR(F^2)$ value for all data was 0.0978. The goodness of fit on F^2 was 1.081. *Crystal data for 4*: $C_{50}H_{26}Fe$, $M = 682.56$, orthorhombic, $a = 37.1090(10)$ Å, $b = 23.2570(10)$ Å, $c = 7.4300(10)$ Å, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 6412.4(9)$ Å³, $T = 100(2)$ K, space group $Pna2_1$, $Z = 8$, synchrotron radiation, 49 378 reflections measured, 12 181 independent reflections ($R_{\text{int}} = 0.0393$). The final R_1 values were 0.0434 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1108 ($I > 2\sigma(I)$). The final R_1 values were 0.0505 (all data). The final $wR(F^2)$ values were 0.1187 (all data). The goodness of fit on F^2 was 1.057.

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