Nanostructures

Electronic Properties of Trifluoromethylated Corannulenes**

Bernd M. Schmidt, Shu Seki, Berit Topolinski, Kei Ohkubo, Shunichi Fukuzumi,
Hidehiro Sakurai, and Dieter Lentz*

More than four decades after the discovery of corannulene[1] (**1**; Figure 1), its chemistry has become multifaceted. Its intrinsic properties have been investigated,[2] and numerous
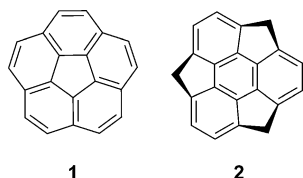

Figure 1. Corannulene (**1**) and sumanene (**2**).

derivatives have been prepared which can be employed, for example, as blue-light emitters,[3] liquid crystals,[4] and synthetic access to isomerically pure armchair carbon nanotube end caps.[5] The solid-state structure of pristine corannulene, which was first investigated in 1976, showed that the solid-state arrangement is dominated by CH···π interactions and a packing without columnar order.[6] Structural variations of the solid-state assembly depend on the substituents attached:[7] Arylalkynyl-substituted corannulenes[8] show an offset but essentially columnar order; bicorannulene on the other hand shows a complex network of π–π and CH···π interactions.[9] Tetrabromocorannulene[8] displays a dense columnar arrangement of the molecular bowls in a convex–concave fashion, which is usually found for bigger buckybowls.[10]

The molecular bowl sumanene (**2**) ($C_{21}H_{12}$) was first synthesized in 2003[11] and its crystal structure was elucidated soon after in 2005.[12] The surprising perfect columnar staggered stacking along the crystallographic *c* axis made **2** a promising material for electrically active organic n-type semiconductors. Consequently, high electron mobility along the molecular stacking axis was measured by time-resolved microwave conductivity methods (TRMC), which implied anisotropic electron-transport properties.[13] In particular, electron-deficient molecules are considered to be promising air-stable organic n-type semiconductors for the construction of thin-film transistors.[14]

This prompted us to design a system that can be utilized for molecular electronics based on the widely explored corannulene buckybowl,[2] which Siegel and co-workers recently succeeded in preparing in kilogram quantities.[15] To tune the electronic properties as well as the self-assembly in the solid state, we chose trifluoromethyl groups as substituents, because of their inherent chemical stability and strong electron-withdrawing properties.[16] First attempts using trifluoromethyl iodide as a trifluoromethylating reagent resulted in complicated mixtures of various compounds (see Figure S1 in the Supporting Information). To avoid this problem, we used a more specific trifluoromethylating agent and introduced the trifluoromethyl groups at specific positions already at an earlier stage of the synthesis.

The first trifluoromethyl group can be introduced by the reaction of the parent corannulene with Togni's reagent (1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one),[17] and compound **3** was isolated in 19% yield (Scheme 1). Since further reaction of **3** would lead to several regioisomers, we opted to introduce two trifluoromethyl groups to the fluoranthene precursor of the corannulene framework. By application of the method published by Siegel and co-workers[18] and those of other groups,[19] the corresponding 1,6,7,10-tetramethyl-8,9-bis(trifluoromethyl)fluoranthene (**4**) was obtained in 76% yield when hexafluorobutyne served as the dienophile.

Fluoranthene **4** can now undergo a Wohl–Ziegler reaction and subsequent nickel-mediated intramolecular coupling[20] to give the *ortho*-bistrifluoromethylated corannulene **6** or can be trifluoromethylated once more to give **5**, which also undergoes the same ring-closing reaction to yield **7**. By this protocol, up to three trifluoromethyl groups can be introduced with high regioselectivity. All of the synthesized compounds were completely characterized and investigated electrochemically in THF solution, using cyclic voltammetry and square-wave measurements. All corannulenes, including **1** (which was measured for comparison), showed one

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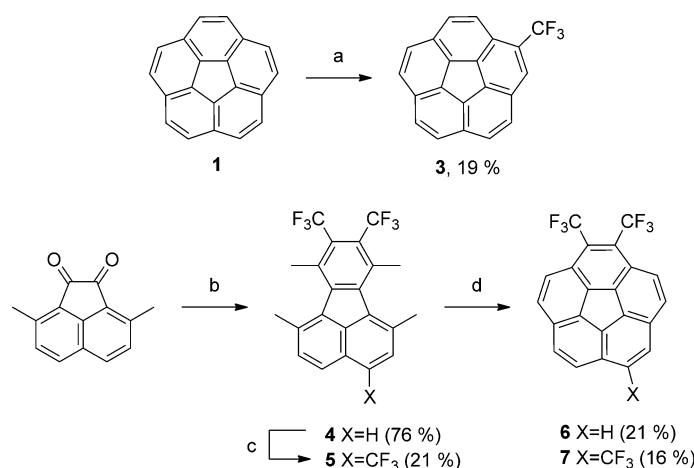E-mail: dieter.lentz@fu-berlin.de

Prof. Dr. S. Seki
Department of Applied Chemistry, Osaka University
2-1 Yamada-oka, Suita, Osaka, 565-0871 (Japan)

B. M. Schmidt, B. Topolinski, H. Sakurai
Research Center for Molecular Scale Nanoscience
Institute for Molecular Science
Myodaiji, Okazaki 444-8787 (Japan)

Dr. K. Ohkubo, Prof. Dr. S. Fukuzumi
Department of Material and Life Science
Graduate School of Engineering, Osaka University
2-1 Yamada-oka, Suita, Osaka, 565-0871 (Japan)

Scheme 1. Synthesis of trifluoromethylated corannulenes. a) 1.0 equiv 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (Togni's acid reagent), 0.1 equiv methyltrioxorhenium, 1,2-dichloroethane, 80°C, 8 h; b) 5.5 equiv pentan-3-one, 1.65 equiv KOH, MeOH, 1 h, RT, then 3.9 equiv hexafluorobutyne, Ac$_2$O, 60°C, 48 h; c) 1.75 equiv 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (Togni's acid reagent), 0.1 equiv methyltrioxorhenium, 1,2-dichloroethane, 80°C, 12 h; d) 12.0 equiv N-bromosuccinimide, 0.03 equiv AIBN (azobisisobutyronitrile), 24 h, 80°C, then 8.8 equiv nickel powder, DMF, 80°C, 8 h.
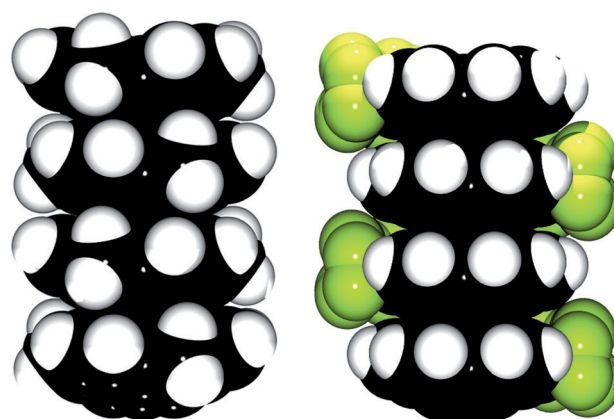

Figure 2. ORTEP[25] representation (space-filling model) of the crystal packing structures, rendered with POV-Ray.[26] Left: A fragment of the extended stack of sumanene (**2**) (C$_{21}$H$_{12}$);[12] intermolecular distance from the centroids of the central six-membered rings 3.86 Å. Right: Fragment of the stacking motif of **6**, showing the concave–convex bowl-in-bowl stacking with an intermolecular distance of 3.73 Å.

reversible reduction.[21] The half-wave reduction potentials are −2.47 for **1**, −2.20 for **3**, −1.86 for **6**, and −1.66 V for **7**, referenced versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple.

As previously reported by the Wang group[22] and the Petrukhina group,[23] the introduction of perfluoroalkyl substituents to an aromatic system shifts the reduction towards higher potentials, hence inducing a stronger electron-accepting ability. Our findings agree with these observations. Already through the introduction of one trifluoromethyl group, the E$_{1/2}$ value of the reduction is shifted by 0.28 V towards higher potentials relative to **1**.

For pentakis(trifluoromethyl)corannulene, Petrukhina and co-workers observed a shift of 0.95 V,[23] which corresponds to a shift of 0.19 V per trifluoromethyl group. Through the selective substitution in specific positions and the resulting lower symmetry, we can increase this shift up to 0.27 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 compound **7** with three trifluoromethyl groups, we observe a shift of 0.82 V compared to **1**; this shift is close to that of pentakis(trifluoromethyl)corannulene (0.95 V).

The solid-state structure of a single crystal of trifluoromethylated corannulene **6** was studied by X-ray diffraction (Figure 2).[24] The molecular bowls of **6** are aligned into parallel columns along the crystallographic c axis, such that neighboring columns are stacked in opposite directions. The bowls have a nearly eclipsed alignment (the central five-membered ring is shifted by 8°). The trifluoromethyl groups, however, are displaced by 140°, as shown in Figure 2, resulting in a densely packed arrangement.

On the basis of the confined columnar stacking structure of **6** in the solid state, we examined the charge-transport

properties in an electrodeless microwave conductivity measurement. Upon excitation at 355 nm, a polycrystalline sample of **6** exhibits a clear signature of photoconductivity as shown in Figure 3a; this is in striking contrast to the conductivity transient observed for amorphous corannulene, which is three orders of magnitude lower. This observation indicates that the corannulene moieties provide a highly electric conductive pathway when they are in an intermolecular π-stacking arrangement analogous to that of crystalline sumanene. Unlike the photoconductivity transient observed in a single crystal of **2**, the transient in crystalline **6** displays
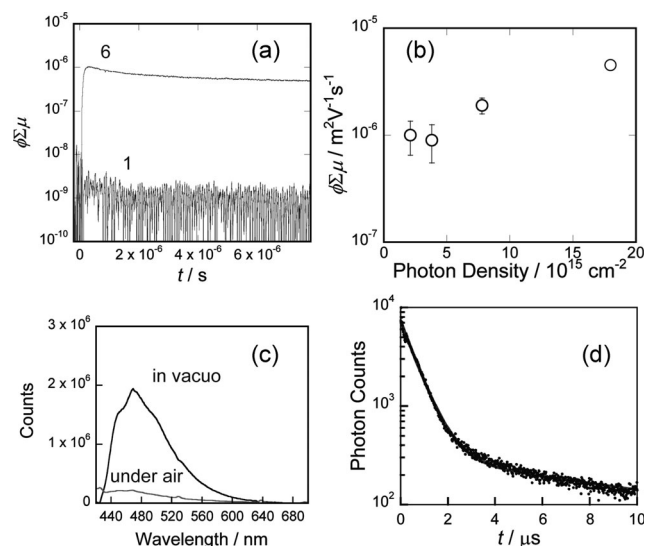
Figure 3. a) Conductivity transients observed for a polycrystalline film of **6** and for a solid film of **1**; excitation at 355 nm, 2.1×10^{15} and 2.8×10^{15} photons cm^{-2}, respectively. b) Dependence of the observed maximum photoconductivity on the excitation photon density. c) Photoinduced emission spectra of **6** upon excitation at 390 nm in vacuo and under air. d) Photoluminescence lifetime measurement of polycrystalline **6** in vacuo with excitation at 390 nm. The emission was observed at 470 nm, 298 K.

a significant delay in the generation of photo-carriers, which is reflected by the considerable increase of transient conductivity over a few µs. The dependence of the maximum value of conductivity (Figure 3b) also supports the second-order generation of photo-carriers through excited-state interactions.

For this reason we examined the contribution of the photoexcited state of **6** to the generation of charge carriers by emission and transient absorption spectroscopy. Considerable photoemission at 468 nm was observed in solid **6** (Figure 3c), and the emission was quenched rapidly by exposure to air. The measurement of the lifetime at 470 nm gives the decay constants of 650 ns and 9.3 µs, suggesting a relatively small energy gap between singlet and triplet excited states of **6**, and especially the latter decay is due to the phosphorescence from the triplet state. The decay constant shows striking contrast to the evolution of transient conductivity in Figure 3a, and this indicates that the free charge carriers in polycrystalline state of **6** are formed predominantly by triplet–triplet annihilation processes in polycrystalline **6**.

Transient absorption spectra of **6** were also observed upon nanosecond laser excitation at 355 nm (Figure S2 in the Supporting Information), giving a clear signature of the formation of the triplet excited state at 400 nm. For quantitative analysis of the yield of the triplet excited state, the transient absorption decay traces were also monitored in a solid film of **6** (Figure S3). Photobleaching of the steady-state absorption was traced at 375 nm, where the molar extinction coefficient of steady-state **6** was $\varepsilon = 4 \times 10^3 \, \mathrm{mol^{-1} dm^3 cm^{-1}}$. The initial photobleaching of the absorption was rapidly recovered within 1 µs, which is mainly due to the relaxation of the singlet excited state with fluorescence. The kinetic trace at 400 nm does not show an initial delay analogous to that of the photobleaching, but decays with the time constant of 3.1 µs, which is in good agreement with the rise time of the conductivity transient. Based on the value of ε at 375 nm, the extinction coefficient of triplet-state **6** (T_1–T_n transition) was estimated as $\varepsilon^t \approx 1.1 \times 10^4 \, \mathrm{mol^{-1} dm^3 cm^{-1}}$. Thus the maximum estimate of the yield of free charge carriers, based on the assumption of 100% conversion of triplet state, has a value ϕ_{max} of 6×10^3. We obtained the minimum limit of charge-carrier mobility as $\Sigma\mu > 0.9 \, \mathrm{cm^2 V^{-1} s^{-1}}$ in **6** (intracolumnar) and $\Sigma\mu > 5 \times 10^{-4} \, \mathrm{cm^2 V^{-1} s^{-1}}$ in **1**. The value for **6** is almost equivalent to that observed for crystalline sumanene.[13]

In summary, we have synthesized trifluoromethylated corannulenes regioselectively by a liquid-phase synthesis and their unprecedented electron-acceptor abilities were investigated in THF solution. Owing to the highly ordered columnar solid-state structure of **6**, it is a highly electrically conductive material with high charge-carrier mobility along the intermolecular stacks. These findings should lead to the development of electrical materials based on corannulenes.

[1] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380–381.

[2] For recent reviews see: a) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843–4867; b) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868–4884; c) A. Sygula, *Eur. J. Org. Chem.* **2011**, 1611–1625.

[3] a) J. Mack, P. Vogel, D. Jones, N. Kaval, A. Sutton, *Org. Biomol. Chem.* **2007**, *5*, 2448–2452; For electroluminescence properties, see: b) L. Zoppi, L. Martin-Samos, K. K. Baldridge, *J. Am. Chem. Soc.* **2011**, *133*, 14002–14009.

[4] D. Miyajima, K. Tashiro, F. Araoka, H. Takezoe, J. Kim, K. Kato, M. Takata, T. Aida, *J. Am. Chem. Soc.* **2009**, *131*, 44–45.

[5] a) L. T. Scott, E. A. Jackson, Q. Zhang, B. D. Steinberg, M. Bancu, B. Li, *J. Am. Chem. Soc.* **2012**, *134*, 107–110; b) S. Schrettl, H. Frauenrath, *Angew. Chem.* **2012**, *124*, 6673–6675; *Angew. Chem. Int. Ed.* **2012**, *51*, 6569–6571; c) C. Thilgen, *Angew. Chem.* **2012**, *124*, 7190–7192; *Angew. Chem. Int. Ed.* **2012**, *51*, 7082–7084.

[6] J. C. Hanson, C. E. Nordman, *Acta Crystallogr. Sect. B* **1976**, *32*, 1147–1153.

[7] Several X-ray structure of rim-substituted corannulenes have been reported, see for example: a) Y. Sevryugina, A. Y. Rogachev, E. A. Jackson, L. T. Scott, M. A. Petrukhina, *J. Org. Chem.* **2006**, *71*, 6615–6618; b) B. Topolinski, B. M. Schmidt, M. Kathan, S. I. Troyanov, D. Lentz, *Chem. Commun.* **2012**, *48*, 6298–6300; c) B. M. Schmidt, B. Topolinski, P. Roesch, D. Lentz, *Chem. Commun.* **2012**, *48*, 6520–6522; d) Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870–6884; for hub-substituted corannulenes, see: e) A. V. Zabula, S. N. Spisak, A. S. Filatov, A. Y. Rogachev, M. A. Petrukhina, *Angew. Chem.* **2011**, *123*, 3027–3030; *Angew. Chem. Int. Ed.* **2011**, *50*, 2971–2974.

[8] a) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **2000**, *122*, 6323–6324; b) Y.-T. Wu, D. Bandera, R. Maag, A. Linden, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **2008**, *130*, 10729–10739.

[9] D. Eisenberg, A. S. Filatov, E. A. Jackson, M. Rabinovitz, M. A. Petrukhina, L. T. Scott, *J. Org. Chem.* **2008**, *73*, 6073–6078.

[10] A. S. Filatov, L. T. Scott, M. A. Petrukhina, *Cryst. Growth Des.* **2010**, *10*, 4607–4621, and references therein.

[11] a) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878–1882; b) S. Higashibayashi, H. Sakurai, *Chem. Lett.* **2011**, *40*, 122–128.

[12] a) H. Sakurai, T. Daiko, S. Hiroyuki, T. Amaya, T. Hirao, *J. Am. Chem. Soc.* **2005**, *127*, 11580–11581; b) S. Mebs, M. Weber, P. Luger, B. M. Schmidt, H. Sakurai, S. Higashibayashi, S. Onogi, D. Lentz, *Org. Biomol. Chem.* **2012**, *10*, 2218–2222.

[13] a) T. Amaya, S. Seki, T. Moriuchi, K. Nakamoto, T. Nakata, H. Sakane, A. Saeki, S. Tagwa, T. Hirao, *J. Am. Chem. Soc.* **2009**, *131*, 408–409; b) S. Higashibayashi, R. Tsuruoka, Y. Soujanya, U. Purushotham, G. N. Sastry, S. Seki, T. Ishikawa, S. Toyota, H. Sakurai, *Bull. Chem. Soc. Jpn.* **2012**, *85*, 450–467.

[14] a) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2012**, *112*, 2208–2267; b) J. Chang, Q. Ye, K.-W. Huang, J. Zhang, Z.-K. Chen, J. Wu, C. Chi, *Org. Lett.* **2012**, *14*, 2964–2967; c) C. Vijayakumar, A. Saeki, S. Seki, *Chem. Asian J.* **2012**, *7*, 1845–1852.

[15] A. M. Butterfield, B. Gilomen, J. S. Siegel, *Org. Process Res. Dev.* **2012**, *16*, 664–676.

[16] S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330.

[17] E. Mejía, A. Togni, *ACS Catal.* **2012**, *2*, 521–527.

[18] a) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921–1923; b) T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7804–7813.

[19] a) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1998**, *120*, 12666 – 12667; b) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1999**, *121*, 7800 – 7803.

[20] A. Sygula, S. D. Karlen, R. Sygula, P. W. Rabideau, *Org. Lett.* **2002**, *4*, 3135 – 3137.

[21] a) C. Bruno, R. Benassi, A. Passalacqua, F. Paolucci, C. Fontanesi, M. Marcaccio, E. A. Jackson, L. T. Scott, *J. Phys. Chem. B* **2009**, *113*, 1954 – 1962; b) T. J. Seiders, K. K. Baldridge, R. Gleiter, J. S. Siegel, *Tetrahedron Lett.* **2000**, *41*, 4519 – 4522; c) K. K. Baldridge, K. I. Hardcastle, T. J. Seiders, J. S. Siegel, *Org. Biomol. Chem.* **2010**, *8*, 53 – 55.

[22] a) Y. Li, C. Li, W. Yue, W. Jiang, R. Kopecek, J. Qu, Z. Wang, *Org. Lett.* **2010**, *12*, 2374 – 2377.

[23] I. V. Kuvychko, S. N. Spisak, Y.-S. Chen, A. A. Popov, M. A. Petrukhina, S. H. Strauss, O. V. Boltalina, *Angew. Chem.* **2012**, *124*, 5023 – 5026; *Angew. Chem. Int. Ed.* **2012**, *51*, 4939 – 4942.

[24] CCDC 892586 (**6**) 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 **6**: $C_{22}H_8F_6$, $M_r = 386.28$, monoclinic, $a = 9.701(3)$, $b = 21.131(6)$, $c = 7.447(2)$ Å, $\alpha = 90.00$, $\beta = 97.645(8)$, $\gamma = 90.00°$, $V = 1513.0(8)$ Å^3, $T = 153(2)$ K, space group $P2_1/c$, $Z = 4$, 6546 reflections measured, 3064 independent reflections ($R_{Int} = 0.0261$). The final R_1 values were 0.0585 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1443 ($I > 2\sigma(I)$). The final R_1 values were 0.0919 (all data). The final $wR(F^2)$ values were 0.1656 (all data).

[25] L. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[26] Persistence of Vision Pty. Ltd. http://povray.org/.

[27] a) S. Seki, S. Tagawa, *Polym. J.* **2007**, *39*, 277 – 293; b) A. Acharya, S. Seki, A. Saeki, Y. Koizumi, S. Tagawa, *Chem. Phys. Lett.* **2005**, *404*, 356 – 360.