Noncovalent Interactions

"Double-Concave" Graphene: Permethoxylated Hexa-*peri*-hexabenzocoronene and Its Cocrystals with Hexafluorobenzene and Fullerene**

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Polycyclic aromatic hydrocarbons (PAHs) represent a unique class of organic molecules since they combine the fascination of fullerene analogues with the outstanding materials properties of graphite and conducting polymers.[1] Their planarity is often presumed to be their most significant geometric characteristic, however, the synthesis of molecules which are at variance with this structural truism has drawn persistent attention from many organic chemists, in particular in view of the total synthesis of fullerene.[2] As a result of the remarkable inner strain of these bent π systems, most of the synthetic routes require extreme conditions such as flash vacuum pyrolysis (FVP), and therefore suffer from low yields and tedious chromatographic separation steps, although a few solution-phase synthesis have been reported.[3]

Recently there has been an increasing interest in supramoleular fullerene chemistry because of its potential applications in chemistry, biology, and materials science.[4] The design of host molecules capable of recognizing fullerenes is mainly based on a kind of complementary principle where the utilization of concave/convex interactions[5] has resulted in the emergence of a few macrocyclic fullerene receptors.[6] Porphyrins and metalloporphyrins with planar π surfaces have also been shown to interact with the curved π surface of fullerenes, predominantly through van der Waals dispersion forces.[7]

The arene–perfluoroarene stacking interactions, which have been shown to occur in numerous 1:1 complexes,[8] are of substantial theoretical and practical importance because of their role in solid-state polymerization,[9a] cross-linking of hydrogels,[9b] molecular electronics[9c] and liquid-crystal stabilization.[9d]

Herein, we introduce a strongly twisted graphene molecule, namely, permethoxylated hexa-*peri*-hexabenzocoronene (permethoxylated HBC, **4**) with a remarkable "double-concave" conformation, as revealed by single-crystal analysis. The combination of a rigid "double-concave" aromatic core with eighteen flexible methoxy groups at the periphery suggests **4** is an ideal model compound for supramolecular host–guest chemistry. Accordingly, we elucidate the single-crystal structures of its crystalline inclusion complexes with hexafluorobenzene (HFB) and fullerene guest molecules, the self-assembly of which is controlled mainly by arene–perfluroarene interactions and geometrically complementary van der Waals interactions, respectively.

Permethoxylated HBC **4** was prepared in three simple steps from commercially available starting materials (Scheme 1). The synthesis of the symmetric 3,3′,4,4′,5,5′-hexamethoxydiphenylacetylene (**2**) was based on a Stille-type coupling of 5-bromo-1,2,3-trimethoxybenzene (**1**) with bis-(tributylstannyl)acetylene. Subsequent cyclotrimerization of the diphenylacetylene with $[Co_2(CO)_8]$ yielded the hexaphenylbenzene precursor molecule **3** bearing 18 alkoxy substituents. The remarkable oxidative cyclodehydrogenation of **3** was carried out under the established ferric chloride conditions.[10] The crude products were purified by column chromatography to yield **4** as an orange solid in 52% yield for the last step (see Supporting Information).

Permethoxylated HBC **4** is the first persubstituted HBC derivative prepared. The additive effect of 18 donor groups to the outer phenyl rings should facilitate an oxidative ring closure whereas the complete substitution of the outer perimeter by alkoxy groups successfully prevents chlorination of the core. The absorption maximum of **4** shows a significant bathochromic shift of 37 nm with respect to the unsubstituted parent HBC as a consequence of the 18 electron-donating alkoxy substituents and the expected nonplanarity caused by steric congestion[11] (see Supporting Information).

To determine the three-dimensional structure of **4**, crystals suitable for single-crystal X-ray structure analysis were obtained by slow evaporation of a solution of **4** in dichloromethane at room temperature.[12] The crystal structure was found to be markedly nonplanar, thus reflecting the presence of pronounced *peri* interactions (Figure 1a). The six carbon atoms of the central benzene ring are coplanar to within 0.014 Å. The steric congestion in the bay region forces the outer aromatic rings to flip up and down in an alternating manner with respect to the inner ring. A similar regular pattern is also observed for the orientation of the methoxy groups which alternately point up and down. The orientation

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Supporting information for this article (the synthesis of compound **4**, packing arrangement of the $[(hfb)_2 \supset \mathbf{4}]$ complex, and UV/Vis absorption spectra of **4**) is available on the WWW under http://www.angewandte.org or from the author.

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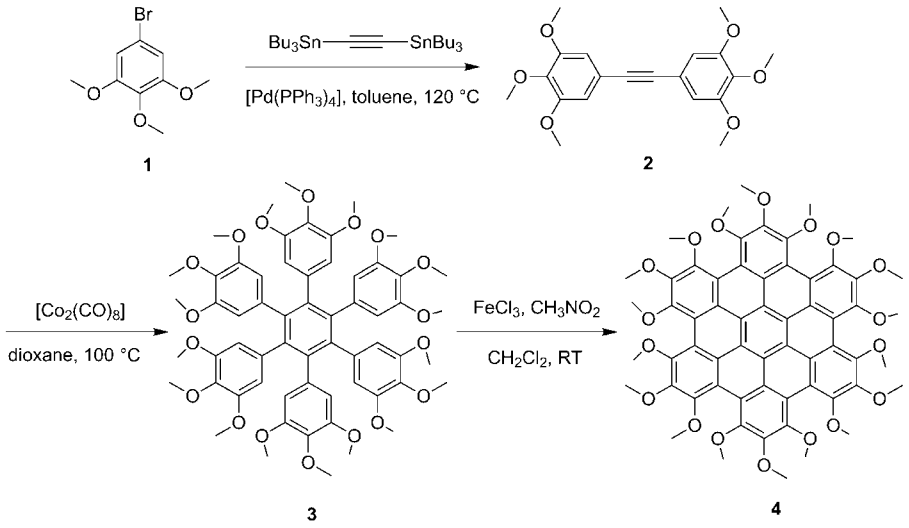

Scheme 1. Synthetic route to permethoxylated HBC (**4**).

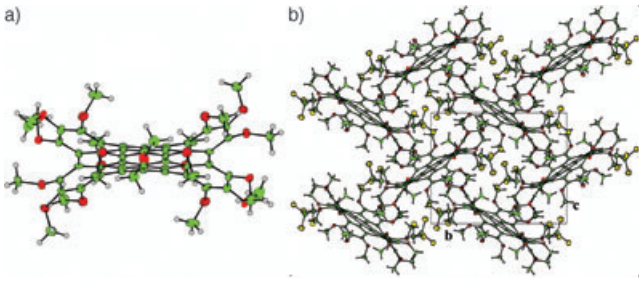

Figure 1. a) Single-crystal structure of **4**; b) herringbone packing arrangement of **4** in the solid state.

of the two *meta*-methoxy groups is found to coincide with that of the twisted phenyl ring, for example, in the case of a phenyl ring flipping down they are oriented in the same direction. The *para*-methoxy group is oriented in the opposite way.

The severe *peri* interactions destabilizing a planar D_{6h} form result in the molecule displaying two concave faces and adopting a centrosymmetric conformation. A similar alternating distortion is observed in perchlorocoronene.[13] In contrast to perchlorocoronene which exhibits only a slight distortion ($\beta = 4.8°$, β is the angle between the central aromatic ring and the distorted outer rings), **4** displays a significant deviation from the planar geometry, with a maximum angle of $\beta = 16.8°$ (for comparison, the fullerene segment corannulene shows an angle of 23.6°).[14]

Permethoxylated HBC (**4**) crystallizes in the common space group $P2_1/c$ and exhibits a herringbone-type structure with a large interplanar distance of 13.05 Å. This packing is quite different from that of parent HBC and hexa-*tert*-butyl-HBC;[15] the 18 overcrowded methoxy groups dramatically change the packing pattern from a face-to-face to an edge-to-face arrangement, since the interplanar distance of **4** is far too large to enable any intermolecular π–π interactions in the crystals (Figure 1 b).

The extraordinary "double-concave" conformation classifies permethoxylated HBC (**4**) as a new host molecule. Inclusion of hexafluorobenzene should be revealing since electron-deficient and electron-rich aromatic rings (for example, HFB and the central coplanar benzene ring of **4**, respectively) have an overwhelming preference for a face-to-face or π-stacked sandwich geometry because of favorable electrostatic quadrupole–quadrupole interactions. Furthermore, a space-filling model shows clearly that HFB fits perfectly into the cavity of **4** (Figure 2).

Crystals of the 2:1 complex $[(hfb)_2 \supset \mathbf{4}]$ possess an asymmetric unit with half a molecule of **4** (on a center of symmetry) and one HFB molecule. HFB and the central ring in **4** are not strictly parallel. As a consequence, the distance of the C atoms of HFB to the plane of **4** ranges from 3.27 to 3.37 Å, and the F atoms of HFB

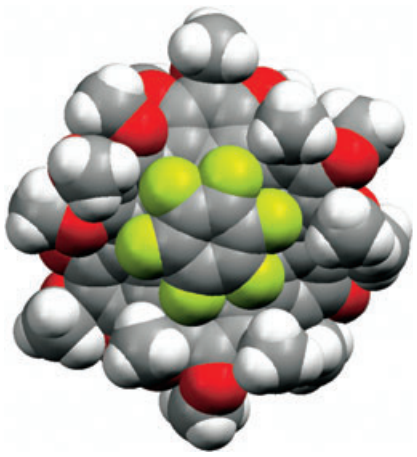

Figure 2. Space-filling model of the complex formed between HFB and **4**.

from 3.15 to 3.43 Å. This distance is closer than the typical stacking separation in arene–perfluoroarene complexes (ca. 3.5 Å), which indicates a strong interaction probably arising from the electron-donating effect of the methoxy groups (Figure 3). Adjacent sandwich complexes are off-set

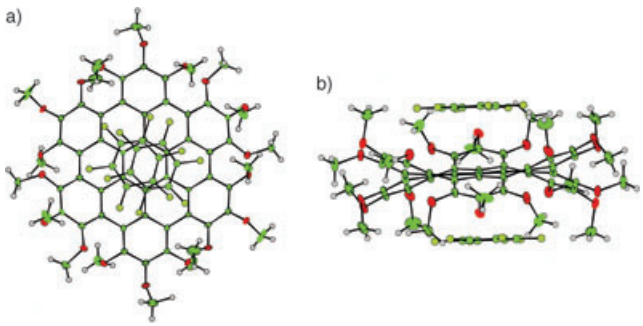

Figure 3. Single-crystal structure of the $[(hfb)_2 \supset \mathbf{4}]$ complex: a) top view and b) side view.

laterally from each other to give a tilted columnar arrangement, in contrast to the normal packing pattern of infinite stacks of alternating arene and perfluoroarene molecules. The close contacts between stacks of complexes consist of F···F interactions between the fluorine atoms at the ends of two neighboring HFB molecules. The F···F separation of 2.79 Å is comparable to a sum of the van der Waals radii of 2.90 Å.[16] This packing preference reflects the combined effect of maximized electrostatic interactions with the two HFB molecules sandwiching the HBC molecules and compatible accommodation of HFB into the cavity formed by flexible surrounding methoxy groups.

The "double-concave" permethoxylated HBC (**4**) was expected to be geometrically complementary to the globular C_{60} shape, and the inclusion of "thick" C_{60} will also afford sufficient separation between HBC molecules and avoid steric crowding of the methoxy groups. Slow evaporation of the solvent from a solution of **4** and fullerene (1:1) in CS_2 yielded black crystals. The crystal structure is shown in Figure 4. The fullerene is positioned exactly on the central

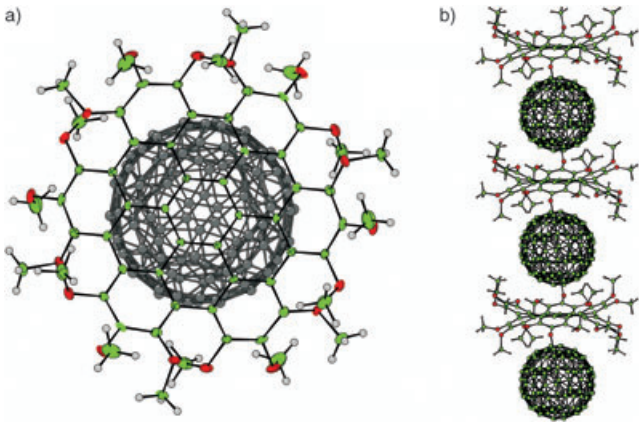

Figure 4. Single-crystal structure of the complex formed between fullerene and **4**: a) top view and b) side view of the columnar packing arrangement.

benzene ring of **4**, thus yielding a perfect columnar packing arrangement. This situation is in contrast to the porphyrin–fullerene complex which shows a zigzag arrangement of porphyrins, with fullerenes sandwiched in the clefts. As is often the case with fullerene structures, there is crystallographic disorder with rapid oscillation of the carbon atoms of the C_{60} molecules;[17] nevertheless, the disposition of **4** and the C_{60} moieties is well resolved.

The closest approach of the C_{60} carbon atoms to the central ring plane of **4** is 2.95 Å, which is significantly shorter than separations observed for normal π–π interactions.[18] The unexpectedly strong interaction between a curved π surface and a flat π surface (central ring of **4**) may be explained in terms of van der Waals interactions and polar electrostatic interactions rather than as charge-transfer interactions.[19]

It should be noted that in addition to the "double-concave" surface which allows the inclusion of suitable guest molecules on both sides, the flexible methoxy groups at the periphery of **4** adjust their orientation to the size and shape of the guest molecules. Indeed, **4** possesses D_{3d} symmetry in the crystals of the fullerene complex, in contrast to the centrosymmetry in its dichloromethane solvates and the HFB complexes. A comparison of the crystal structures shows that the orientation of the 18 methoxy groups changes to provide a cavity into which the different guest molecules may be accommodated.

We have presented a novel approach to an extremely nonplanar persubstituted HBC derivative by using the facile cyclodehydrogenation procedure with ferric chloride at room temperature. X-ray single-crystal analysis revealed that permethoxylated HBC (**4**) has an extraordinary "double-concave" conformation in which the dramatic deviation from planarity arises because of steric congestion in the bay region. The remarkable propensity of guest molecules to change the self-assembly of this novel host molecule and the fascinating structures obtained in this way are intriguing in view of the design of new host–guest systems and materials, for example, based on functionalized fullerenes and perfluoroarenes. Attaching long alkyl chains onto the PAH core should give it liquid-crystalline properties.

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[1] a) E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, **1964**; b) M. Zander, *Polycyclische Aromaten*, B. G. Teubner, Stuttgart, **1995**.

[2] a) Examples of nonplanar PAHs: S. Grimme, J. Harren, A. Sobanski, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1491; K. Shibata, A. A. Kulkarni, D. M. Ho, R. A. Pascal, Jr., *J. Am. Chem. Soc.* **1994**, *116*, 5983; R. A. Pascal, Jr., W. D. McMillan, D. V. Engen, R. G. Eason, *J. Am. Chem. Soc.* **1987**, *109*, 4660; H. M. Duong, M. Bendikov, D. Steiger, Q. Zhang, G. Sonmez, J. Yamada, F. Wudl, *Org. Lett.* **2003**, *5*, 4433; N. Kobayashi, T. Fukuda, K. Ueno, H. Ogino, *J. Am. Chem. Soc.* **2001**, *123*, 10740; b) for the total synthesis of fullerene and the synthesis of the bowl-shaped fullerene segment corannulene, see, for example: M. M. Boorum, Y. V. Vasil'ev, T. Drewello, L. T. Scott, *Science* **2001**, *294*, 828; H. E. Bronstein, N. Choi, L. T. Scott, *J. Am. Chem. Soc.* **2002**, *124*, 8870; T. J. Seiders, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7804; R. G. Lawton, W. E. Barth, *J. Am. Chem. Soc.* **1971**, *93*, 1730.

[3] a) T. J. Seiders, K. K. Baldrige, J. S. Siegel, *J. Am. Chem. Soc.* **1996**, *118*, 2574; b) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **2000**, *122*, 6323; c) H. A. Reisch, M. Bratcher, L. T. Scott, *Org. Lett.* **2000**, *2*, 1427.

[4] A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**; F. Diederich, C. Thilgen, *Science* **1996**, *271*, 317; A. Hirsh, *Angew. Chem.* **2004**, *116*, 2380; *Angew. Chem. Int. Ed.* **2004**, *43*, 2326; F. Diederich, M. Gomez-Lopez, *Chem. Soc. Rev.* **1999**, *28*, 263; J. F. Nierengarten, *Top. Curr. Chem.* **2003**, *228*, 87; J. F. Nierengarten, *Angew. Chem.* **2001**, *113*, 3061; *Angew. Chem. Int. Ed.* **2001**, *40*, 2973.

[5] F. Hajek, M. W. Hosseini, E. Graf, A. De Cian, J. Fischer, *Angew. Chem.* **1997**, *109*, 1830; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1760.

[6] For examples, see: J. L. Atwood, G. A. Koutsantonis, C. L. Raston, *Nature* **1994**, *368*, 229; T. Suzuki, K. Nakashima, S. Shinkai, *Chem. Lett.* **1994**, 699; T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1998**, *110*, 1044; *Angew. Chem. Int. Ed.* **1998**, *37*, 997; J. L. Atwood, L. J. Barbour, C. L. Raston, I. B. N. Sudria, *Angew. Chem.* **1998**, *110*, 1029; *Angew. Chem. Int. Ed.* **1998**, *37*, 981; T. Kawase, K. Tanaka, N. Fujiwara, H. R. Darabi, M. Oda, *Angew. Chem.* **2003**, *115*, 1662; *Angew. Chem. Int. Ed.* **2003**, *42*, 1624; M. Wang, X. Zhang, Q. Zheng, *Angew. Chem.* **2004**, *116*, 856; *Angew. Chem. Int. Ed.* **2004**, *43*, 838.

[7] a) Y. Sun, T. Drovetskaya, R. D. Bolskar, R. Bau, P. D. W. Boyd, C. A. Reed, *J. Org. Chem.* **1997**, *62*, 3642; b) M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar, A. L. Balch, *J. Am. Chem. Soc.* **1999**, *121*, 7090; c) P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **1999**, *121*, 10487.

[8] For reviews and examples, see: E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1224; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210; J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, T. B. Marder, *New J. Chem.* **2001**, *25*, 1410; M. Gdaniec, W. Jankowski, M. J. Milewska, T. Polonski, *Angew. Chem.* **2003**, *115*, 4033; *Angew. Chem. Int. Ed.* **2003**, *42*, 3903; S. W. Watt, C. Dai, A. J. Scott, J. M. Burke, R. Ll. Thomas, J. C. Collings, C. Vieney, W. Clegg, T. B. Marder *Angew. Chem.* **2004**, *116*, 3123; *Angew. Chem. Int. Ed.* **2004**, *43*, 3061.

[9] a) G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty, R. H. Grubbs, *Angew. Chem.* **1997**, *109*, 290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 248; G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 3641; b) A. F. M. Kilbinger, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 1633; *Angew. Chem. Int. Ed.* **2002**, *41*, 1563; c) M. L. Renak, G. P. Bartholomeu, S. Wang, P. J. Ricatto, R. J. Lachiotte, G. C. Bazan, *J. Am. Chem. Soc.* **1999**, *121*, 7787; W. J. Feast, P. W. Lovenlich, H. Puschmann, C. Taliani, *Chem. Commun.* **2001**, 505; d) M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky, R. H. Grubbs, *Angew. Chem.* **1999**, *111*, 2909; *Angew. Chem. Int. Ed.* **1999**, *38*, 2741.

[10] a) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; b) Z. Wang, M. D. Watson, J. Wu, K. Müllen, *Chem. Commun.* **2004**, 336.

[11] Z. Wang, Z. Tomovic, M. Kastler, R. Pretsch, F. Negri, V. Enkelmann, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 7794.

[12] Data collections for the crystal-structure analysis were performed on a Nonius KCCD diffractometer equipped with a Cryostream cooler with graphite monochromated Mo*K*a radiation. The structures were solved by direct methods (Shelxs) and refined on *F* with anisotropic temperature factors for the non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. **4**·4 CH_2Cl_2: $C_{32}H_{31}Cl_4O_9$, monoclinic, space group $P2_1/c$, $T = 150$ K, $a = 14.6101(7)$, $b = 13.0471(6)$, $c = 16.2439(7)$ Å, $\beta = 91.990(3)°$, $V = 3094.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.505$ g cm^{-3}, $\mu = 0.438$ mm^{-1}; 12418 reflections measured, of which 7485 were unique ($R_{int} = 0.026$) and 3661 were observed; $R = 0.086$, $R_w = 0.0817$. **4**·2 C_6F_6: $C_{36}H_{27}F_6O_9$, triclinic, space group $P\bar{1}$, $T = 120$ K, $a = 11.1105(5)$, $b = 11.7330(5)$, $c = 13.0297(6)$ Å, $\alpha = 73.425(1)$, $\beta = 88.923(1)$, $\gamma = 75.098(1)°$, $V = 1570.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.517$ g cm^{-3}, $\mu = 0.131$ mm^{-1}; 29594 reflections measured, of which 8552 were unique ($R_{int} = 0.048$) and 5203 were observed; $R = 0.0651$, $R_w = 0.0698$. **4**·C_{60}: $C_{20}H_9O_3$, trigonal, space group $R\bar{3}$, $T = 120$ K, $a = 22.1940(7)$, $b = 22.1940(7)$, $c = 12.8191(5)$ Å, $V = 5468.4(6)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.624$ g cm^{-3}, $\mu = 0.110$ mm^{-1}; 26529 reflections measured, of which 3375 were unique ($R_{int} = 0.041$) and 1687 were observed; $R = 0.0872$, $R_w = 0.0967$. The fullerene molecule was found to be disordered even at low temperatures such that no meaningfull bonding geometry could be detected in the fullerene fragment. The strongest peaks observed in difference fourier maps were included in the refinement. In the initial refinement cycles they were refined with a common isotropic temperature factor and variable occupancy factors. Additional difference fourier peaks were added until the electron density in the C_{60} fragment amounted to the expected value of 10 carbon atoms. In the last cycles of the refinement they were refined with isotropic temperature factors and the fixed occupancy factors which had been determined in the previous refinement cycles. CCDC-245390, CCDC-245391, and CCDC-245392 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] a) T. Baird, J. H. Gall, D. D. MacNicol, P. R. Mallinson, C. R. Michie, *J. Chem. Soc. Chem. Commun.* **1988**, 1471; b) G. A. Downing, C. S. Frampton, D. D. MacNicol, P. R. Mallinson, *Angew. Chem.* **1994**, *106*, 1653; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1587.

[14] J. C. Hanson, C. E. Nordmann, *Acta Crystallogr. Sect. B* **1975**, *32*, 1147.

[15] a) R. Goddard, M. W. Haenel, W. C. Herndon, C. Krüger, M. Zander, *J. Am. Chem. Soc.* **1995**, *117*, 30; b) P. T. Herwig, V. Enkelmann, O. Schmelz, K. Müllen, *Chem. Eur. J.* **2000**, *6*, 1834.

[16] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384.

[17] B. Narymbetov, H. Kobayashi, M. Tokumoto, A. Omerzu, D. Mihailovic, *Chem. Commun.* **1999**, 1511.

[18] Graphite and typical arene/arene separation is in the range 3.3–3.5 Å, fullerene/arene approaches lie in the range 3.0–3.5 Å, calixarene/fullerene and related complexes 3.5–3.6 Å, however, a close approach 2.75 Å is observed for a porphyrin/fullerene assembly.[7]

[19] A toluene solution of C_{60} and **4** shows UV/Vis spectra that are simply the superposition of the spectra of the two individual chromophores without a charge-transfer absorption band; however, it is still difficult to draw conclusions about whether or not charge-transfer interactions are important in crystals

