Angewandte Chemie International Edition

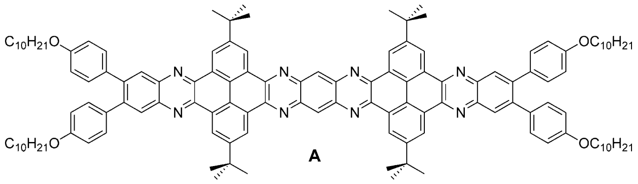
Polycyclic π Systems

International Edition: DOI: 10.1002/anie.201411972
German Edition: DOI: 10.1002/ange.201411972

A Pyrene-Fused *N*-Heteroacene with Eleven Rectilinearly Annulated Aromatic Rings**

*Bernd Kohl, Frank Rominger, and Michael Mastalerz**

Abstract: *A highly soluble pyrene-fused undecacene is realized by end-capping the rectilinear aromatic π-plane with triptycenylene units. Besides the good solubility, the compound shows a high tendency to crystallize. Two polymorphs from dichlorobenzene and chloroform are described. In the polymorph from chloroform, half of the molecules are strongly bent out of the π-plane by 26.4°.*



A

Figure 1. A soluble pyrene-fused pyrazaacene (PFP) with 11 rectilinearly fused six-membered aromatic rings.[14]

Extended fused polycyclic π-systems are interesting compounds in respect to organic electronics, but also to get a deeper insight into aromaticity and stability of π-systems generally.[1,2] For instance the non-substituted higher homologues of the linearly fused [*n*]acenes with $n \geq 6$ (such as heptacene, octacene, and nonacene) are prone of photo-oxidation or photo-dimerization and have exclusively been investigated by matrix-isolation techniques.[3] According to the concept of Clar[4] only one sextet can be drawn in the molecular structure, which explains the photophysical as well as chemical behavior as a polyene rather than as a 'polybenzoid' compound. One possibility to prevent decomposition is the introduction of bulky or electron-withdrawing groups to the acene scaffold.[5–7] With this strategy, higher acenes as well as *N*-heteroacenes, such as azahexacenes and azaheptacenes, have been synthesized.[8]

In contrast to the linearly fused acenes, pyrene containing structures are much more stable owing to the cross-conjugated character of the pyrene unit.[9–12] Although not structurally defined, polymers containing these pyrene-fused pyrazaacenes (PFPs) have been prepared, which have been reported to be highly stable, for example, when heated over 500 °C in air.[13] By vapor pressure osmosis it was suggested that these polymers have a molecular weight of approximately 7000 g mol^{-1}, thus, containing up to 85(!) linearly fused aromatic six-membered rings. Structurally more defined and monodisperse larger PFPs have been introduced by Wang and co-workers, who were able to synthesize PFPs with up to 16 rectilinearly arranged, fused aromatic six-membered rings.[14] To enhance the solubility, *tert*-butyl groups were attached at the pyrene units and *para*-alkoxyphenyl substituents with long alkyl chains ($C_{10}H_{21}$) were introduced at the longitude peripheral ends of the PFPs (see Figure 1). Despite its better solubility comparing to non-substituted PFPs, PFP **A** already shows very broad peaks in the ^{1}H NMR spectrum suggesting a strong π–π stacking in solution (see below). Unfortunately, only for the smallest member of this series, were crystals suitable for X-ray diffraction obtained.[14,15]

During our ongoing work on triptycene-based extended D_{3h}-symmetric π-systems by condensation of pyrene tetraketones and triptycene hexaammonium salts,[16] we recognized that a derivative end-capped with triptycenylene moieties is notably more soluble than those with, for example, phenylene moieties. Swager et al. have already used a similar concept and introduced the iptycene moiety into conjugated polymers to enhance solubility and optical effects.[17] Therefore we were curious whether this type of substitution pattern is sufficient to increase the solubility of longer PFPs, such as **4**, with eleven rectilinearly annulated aromatic rings.

The synthesis is outlined in Scheme 1. Pyrene tetraketone **1** was condensed with triptycene diammonium salt **2**, whereas the ketone was used in access to get the diketo compound **3** selectively in good yields of 76%. The excess of tetraketone can be easily recycled by extraction with hot methanol and reused again. Diketone **3** is treated with the commercially available 1,2,4,5-tetraammoniumbenzene tetrachloride, giving the PFP **4** in yields of 22%.

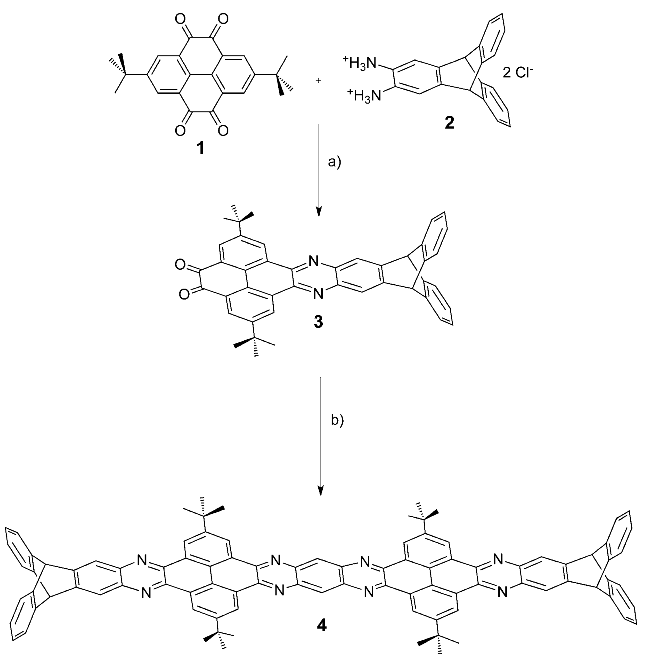
The ^{1}H NMR spectrum of **4** shows, in contrast to extended PFP **A**, well-resolved signals in deuterochloroform at room temperature (298 K) even at higher concentrations (6 mg mL^{-1}), thus suggesting that the compound is molecularly dissolved (see Supporting Information). In comparison, a ^{1}H NMR spectrum of PFP **A** with very broad peaks has been recorded in *ortho*-[D_4]dichlorbenzene at 373 K.[14] This result means that end-capping oligoacenes with triptycenylene units is more efficient at enhancing solubility than attaching long alkoxy chains. Furthermore, the extinction coefficient measured by UV/Vis spectroscopy is not changing with varying concentrations of solutions of **4**, again giving an indication for a molecular dissolved species. The UV/Vis spectrum of PFP **4** is comparable with PFP **A**, showing bands at $\lambda = 522$, 489, 461 nm which are assigned to the transitions 0-0, 0-1, and 0-2

---

[*] Dipl.-Chem. B. Kohl, Dr. F. Rominger, Prof. Dr. M. Mastalerz
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 273, 69120 Heidelberg (Germany)
E-mail: michael.mastalerz@oci.uni-heidelberg.de

[**] We thank the Deutsche Forschungsgemeinschaft and Fond der Chemischen Industrie for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411972.



Scheme 1. Synthesis of undecacene **4**. a) $CHCl_3$, AcOH, KOAc, 70 °C, 16 h, 76 % yield; b) 1,2,4,5-tetraammoniumbenzene tetrachloride, $CHCl_3$, AcOH, KOAc, 70 °C, 24 h, 22 % yield.

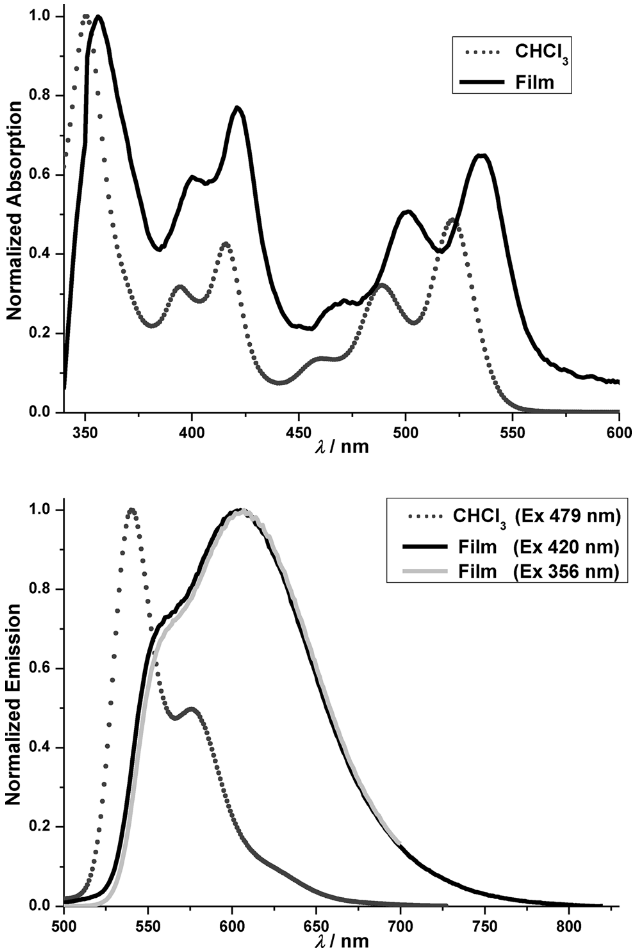


Figure 2. Top: Normalized UV/Vis absorption spectra of **4** in solution (chloroform, 6×10^{-6} M) and thin film measured at room temperature. Bottom: Normalized fluorescence spectra of **4** in solution (chloroform, 1×10^{-6} M) and thin film at room temperature.

(Figure 2). Whether irradiated at $\lambda = 351$ nm or 479 nm, the compound showed the same emission at $\lambda = 540$ and 576 nm and a shoulder at approximately 610 nm. The Stokes shift of 18 nm suggests a small reorganization energy for the transition of the ground state to the first excited state. In thin films spin coated from toluene as solvent, the absorption peaks are shifted about 10–12 nm bathochromically. For instance, the absorption band at $\lambda = 522$ nm is red-shifted to 534 nm. However the peaks are not substantially broadened to those observed in solution. The emission of the film is clearly bathochromically shifted, giving a broad band at $\lambda = 607$ nm, independent whether irradiated at $\lambda = 420$ or 356 nm. This situation is probably due to the formation of excimers.

By cyclovoltammetry (CV) three distinct reversible reduction waves at $E_{1/2} = -1.4$ V, −1.8 V, and −2.3 V have been measured (see Supporting Information). The LUMO level calculated from CV data is at $E_{\mathrm{LUMO}} = -3.8$ eV.

Single-crystals of undecacene **4**, suitable for analysis by X-ray diffraction, have been grown from *ortho*-dichlorobenzene (oDCB) or chloroform. The crystals from oDCB and chloroform show different types of arrangement of the undecacene molecules **4**.

The crystals obtained from oDCB were of high quality, so that bond lengths and angles of **4** can accurately be described (see Figure 3). Most interestingly, with the exception of the two peri-annulated phenyl rings of the pyrene unit, the bonds within the six-membered rings show clearly alternating lengths. For instance, the phenylene ring of the triptycenyl unit, which is part of the undecacene, shows a more pronounced alternation with relative short bond lengths between C21 and C22 ($d = 1.35$ Å) or C23 and C24 ($d = 1.36$ Å) rather than a delocalized character. The π-system of the undecacene is nearly perfectly planar and shows only slight bending or twisting. The length measured between two bridgehead units of the triptycenylene end-caps is 29.1 Å. The molecules of **4** form sheets by a slightly offset aggregation where the four *tert*-butyl groups of two adjacent molecules are placed in the "bays" between the pyrene units, as a result of multiple dispersion interactions. The sheets are lying on top of each other, building voids between the π-planes with a distance $d(\pi\cdots\pi)$ between 6.8 and 6.9 Å, and in the voids two coplanarly arranged dichlorobenzene molecules are located nearly exactly on half distance, so that the crystal lattice is stabilized by π–π stacking between undecacene **4** and oDCB. In contrast to the crystals grown from oDCB, those from $CHCl_3$ have two independent molecules in the asymmetric unit (Figure 4). One molecule (**4^{A}**) is nearly planar, having a very slight *S*-type deformation of the π plane. Most interestingly, a similar sheet-like motif of **4^{A}** is found as in the oDCB polymorph. But, instead of solvent molecules localized in the voids between the sheet structures of **4^{A}**, in this case two molecules of **4^{B}**, themselves interacting by strong π–π stacking interactions, are enclathrated. Molecules **4^{B}** are clearly bent about 26.4° and wrap around **4^{A}** in a way that the end-capping triptycenylene unit of **4^{B}** is placed between two

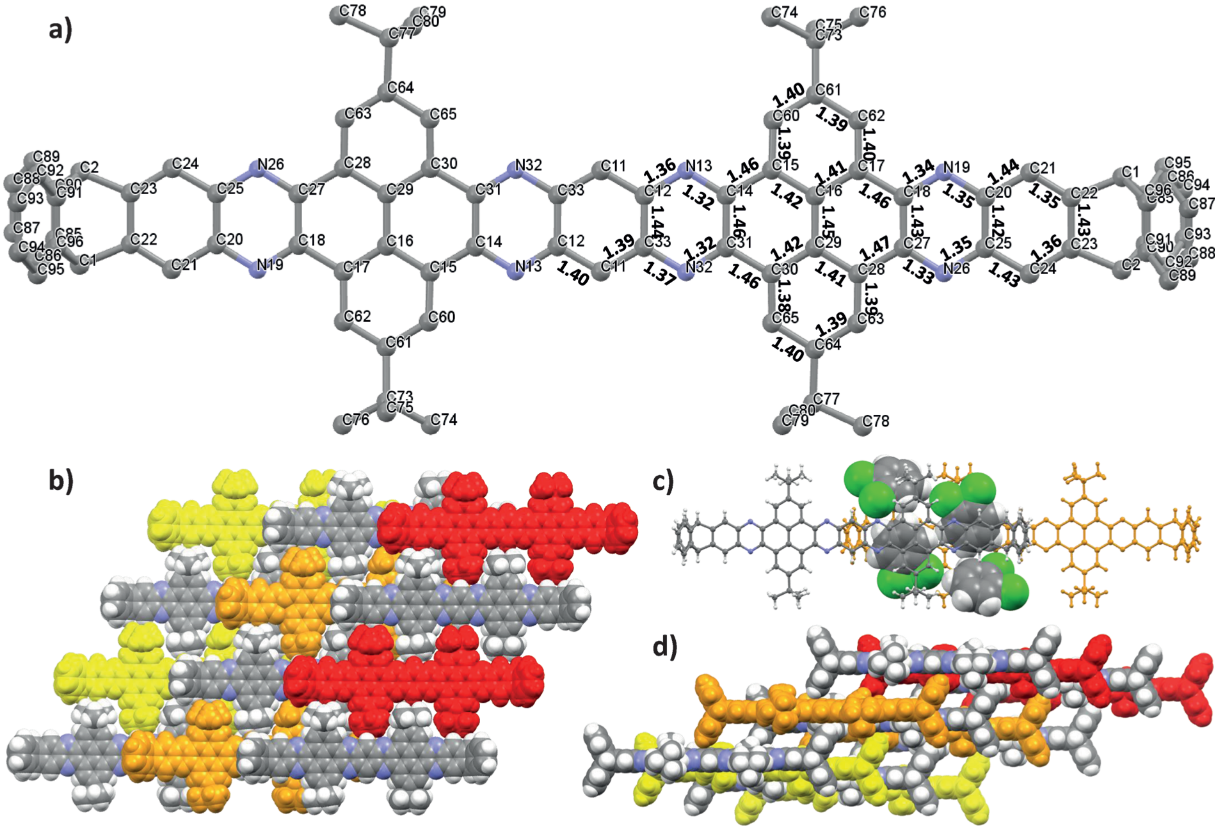


Figure 3. Single-crystal X-ray structure of crystals grown from oDCB. a) molecular structure, bond lengths in [Å]. b) packing along the crystallographic *b*-axis. To highlight the packing motif, every second molecule is depicted in a single color. c) enclathrated oDCB molecules (depicted as space-filling models) in the crystal voids of two adjacent undecacenes **4** (ball and stick model). d) packing along the crystallographic *a*-axis.

tert-butyl groups of the adjacent molecule $\mathbf{4^A}$. The shortest distance between the π-planes of two molecules $\mathbf{4^B}$ is very short with 3.31 Å. The deviation from planarity of $\mathbf{4^B}$ is further stabilized by additional π–π and CH–π stacking of the aromatic phenylene units of the triptycenylene moieties with the π-plane of the undecacene core unit of an adjacent molecule $\mathbf{4^B}$ (shortest distance between two carbon atoms is 3.19 Å). The enclathrated chloroform molecules are located in large zigzag channels in a disordered fashion and could not be refined.

The significant deviation of the π-plane of $\mathbf{4^B}$ occurred when no solvent molecules (such as oDCB) are enclathrated into the crystal lattice, which are able to contribute in crystal stabilization by π–π stacking. There have been some larger π-systems described by single-crystal X-ray diffraction, in which the molecular surface is twisted or bent. However, in all those cases this is more likely because the steric demands of peripheral atoms forcing the system to deviate from planarity.[18] To our knowledge, this has not been described for extended fused π-systems without molecular steric stress.[19,20]

A reasonable explanation for the bending is the increased lattice energy of the crystal by additional dispersion interactions. Although without precedent, Grimme and Bettinger theoretically predicted a deviation of π-planes in a [4+4]-cycloadduct of a nonacene, forced by attractive dispersion interactions,[21] similar to what has been observed by us.

In the solid state compound **4** is stable for several weeks and showed no decomposition: we observed no changes in recorded NMR spectra of **4** stored as a powder without any precautions (e.g. preservation from light or air) even after four months. In solution, the ^{1}H NMR spectrum is nearly unchanged for several days provided the solution is kept strictly away from a light source. However, in contrast of previous observations on PFPs,[13,14] we found that after 35 days a slow degradation of **4** to the quinone **5** had taken place, when the NMR tube was stored without any precautions and light was accessible to the sample (see Supporting Information). The quinone structure has been confirmed by NMR, IR, UV/Vis spectroscopy and mass spectrometry, as well by comparison of the analytical data to the synthesized compound **5** from tetraaminoquinone **6** and diketone **3**, which are in total agreement to the ones of the isolated decomposition product (Scheme 2, see also Supporting Information).

To conclude, we have described the synthesis of an aromatic system with 11 rectilinear fused six-membered rings, which is highly soluble and at the same time shows a high tendency to form single-crystals. To our knowledge, this is the longest linearly fused aromatic system that has been characterized by X-ray diffraction.[22] Most interestingly, triptycenylene end-caps at both ends of the aromatic undecacene are sufficient enough to enhance the solubility of the compound tremendously and seem to be superior to long linear alkyl

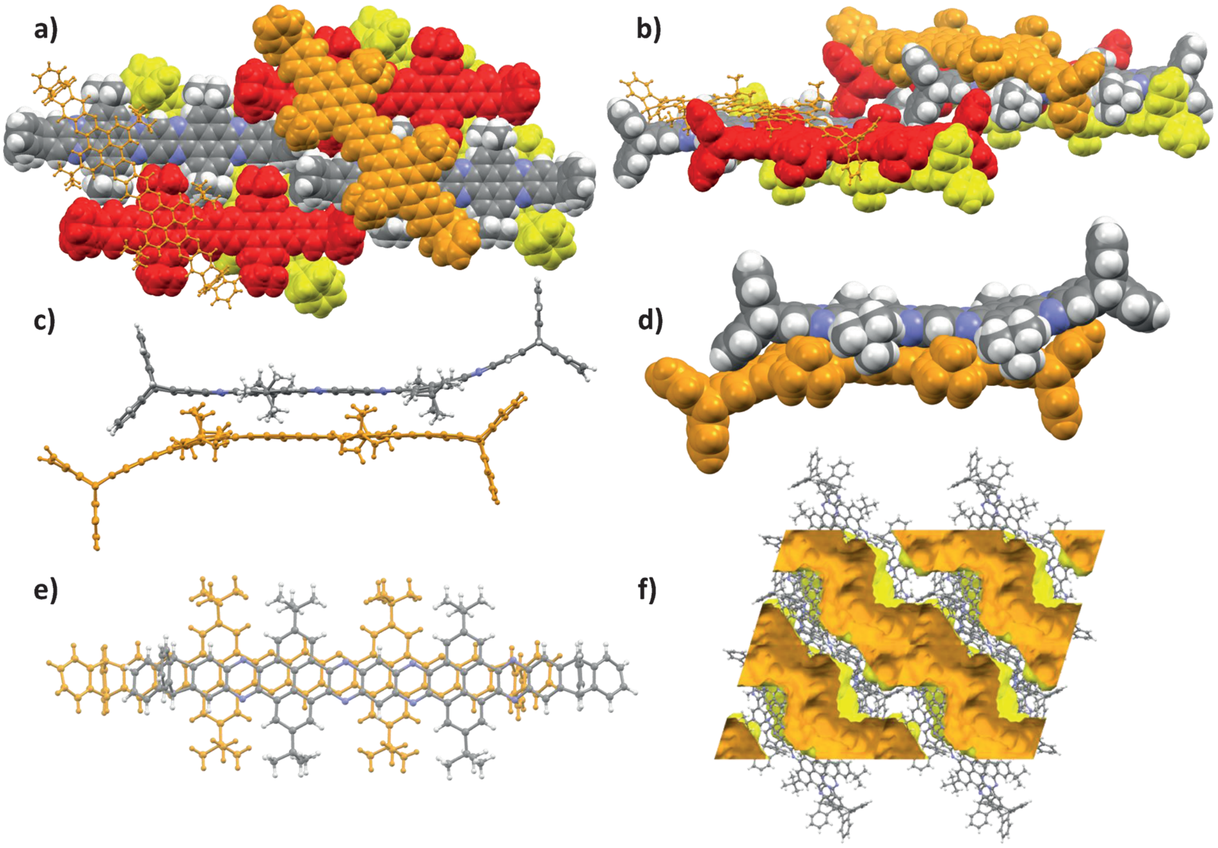
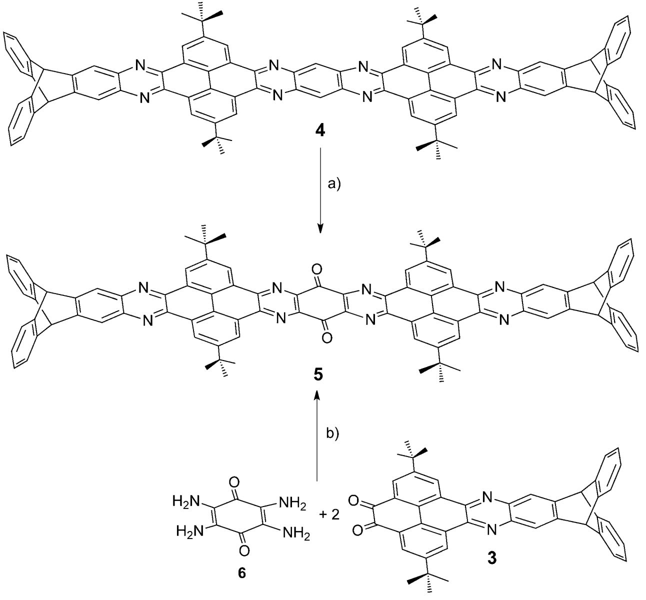


Figure 4. Single-crystal X-ray structure of crystals of **4** grown from $CHCl_3$. a) and b) packing along a non-defined axis. Molecules $\mathbf{4}^A$ in red and elemental colors showing the sheet-like structure similar to that in the polymorph crystallized from oDCB. Molecules $\mathbf{4}^B$ are yellow or orange. One molecule $\mathbf{4}^B$ is shown as ball-and-stick-model to highlight the bent–wrapping motif. c)–e) π–π stacking of two adjacent molecules $\mathbf{4}^B$. f) Pore structure. Inside the pores (orange surface) disordered $CHCl_3$ molecules are enclathrated. For clarity reasons in (a) and (b) only the interaction of one molecule $\mathbf{4}^B$ with adjacent molecules $\mathbf{4}^A$ is depicted and no dimers $\mathbf{4}^B\cdot\mathbf{4}^B$.



Scheme 2. a) Oxidation of **4** in $CDCl_3$ solution under laboratory illumination. b) condensation in $CHCl_3$, AcOH, 70 °C, 24 h.

chains. We will further explore the possibilities to "substitute" solubilizing alkyl chains[23] for end-capping triptycenyl units on even longer PFPs and other π-systems, which are usually of very low solubility, but have interesting optoelectronic properties.

Experimental Section

For synthetic procedures and full characterization of compounds **3**, **4**, and **5** see Supporting Information. Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation from a dilute $CHCl_3$ ($0.5\ \mathrm{mg\,mL^{-1}}$) solution of **4** and by slow evaporation of a saturated *ortho*-dichlorobenzene solution of **4**. Data were collected at 200 K on a Bruker APEX-II Quazar with a Mo-K_α radiation ($\lambda = 0.71073$ Å). Data processing and absorption correction (SADABS)[24] were accomplished by standard methods. The structure was solved by direct methods and refined by full-matrix least-squares using SHELXL software.[25] All non-hydrogen atoms were refined using anisotropic thermal parameters, hydrogen atoms were treated using appropriate riding models.

Crystal data for **4** crystallized from $CHCl_3$: $T = 200(2)$ K, $C_{94}H_{70}N_8$, $M_r = 1311.58$, triclinic space group $P\bar{1}$, $Z = 4$, $a = 19.147(6)$, $b = 20.818(7)$, $c = 26.276(9)$ Å, $\alpha = 104.155(8)$, $\beta = 106.234(8)$, $\gamma = 92.153(9)°$, $V = 9687(6)$ Å^3, $\rho_{calcd} = 0.90\ \mathrm{g\,cm^{-3}}$, $\mu = 0.05\ \mathrm{mm^{-1}}$, $0.8° < \theta < 13.6°$, reflections collected/unique 16066/5594 [$R(\mathrm{int}) = 0.1118$], data/restrains/parameters 5594/3406/817 GOF 1.47, final $R[I > 2\sigma(I)]$ $R1 = 0.152$, wR2 (all data) = 0.391, residual density 0.49 and −0.39 e Å^{-3}.

Crystal data for **4** crystallized from oDCB: $T = 200(2)$ K, $C_{130}H_{94}Cl_{12}N_8$, $M_r = 2193.53$, triclinic space group $P\bar{1}$, $Z = 1$, $a = 12.6319(10)$, $b = 13.7783(11)$, $c = 16.8980(14)$ Å, $\alpha = 99.765(1)$, $\beta = 109.587(1)$, $\gamma = 93.707(1)°$, $V = 2707.2(4)$ Å^3, $\rho_{calcd} = 1.35$ g cm^{-3}, $\mu = 0.36$ mm^{-1}, $1.3° < \theta < 24.1°$, reflections collected/unique 38702/8591 [R(int) = 0.0670], data/restrains/parameters 8591/2382/790 GOF 1.07, final $R[I > 2\sigma(I)]$ $R1 = 0.104$, wR2 (all data) = 0.292, residual density 1.01 and −0.81 e Å^{-3}.

CCDC 1038238 (**4** from $CHCl_3$) and 1038239 (**4** from oDCB) contain 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.

Keywords: dispersion interactions · N-acenes · polymorphism · pyrenes · structure elucidation

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 6051–6056
Angew. Chem. **2015**, *127*, 6149–6154

---

[1] a) A. C. Grimsdale, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5592–5629; *Angew. Chem.* **2005**, *117*, 5732–5772; b) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267–1300.

[2] a) K. J. Thorley, J. E. Anthony, *Isr. J. Chem.* **2014**, *54*, 642–649; b) M. Watanabe, K. Y. Chen, Y. J. Chang, T. J. Chow, *Acc. Chem. Res.* **2013**, *46*, 1606–1615; c) Q. Ye, C. Chi, *Chem. Mater.* **2014**, *26*, 4046–4056; d) H. F. Bettinger, C. Tönshoff, *Chem. Rec.* **2015**, *15*, 364–369; e) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483; *Angew. Chem.* **2008**, *120*, 460–492; f) M. Bendikov, F. Wudl, D. F. Peripichka, *Chem. Rev.* **2004**, *104*, 4891–4946; g) S. S. Zade, M. Bendikov, *Angew. Chem. Int. Ed.* **2010**, *49*, 4012–4015; *Angew. Chem.* **2010**, *122*, 4104–4107.

[3] a) R. Mondal, B. K. Shah, D. C. Neckers, *J. Am. Chem. Soc.* **2006**, *128*, 9612–9613; b) H. F. Bettinger, R. Mondal, D. C. Neckers, *Chem. Commun.* **2007**, 5209–5211; c) R. Mondal, C. Tönshoff, D. Khon, D. C. Neckers, H. F. Bettinger, *J. Am. Chem. Soc.* **2009**, *131*, 14281–14289; d) C. Tönshoff, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2010**, *49*, 4125–4128; *Angew. Chem.* **2010**, *122*, 4219–4222; e) R. Einholz, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2013**, *52*, 9818–9820; *Angew. Chem.* **2013**, *125*, 10000–10003.

[4] E. Clar, *The Aromatic Sextet*, Wiley, New York, **1972**.

[5] a) B. Purushothaman, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2010**, *12*, 2060–2063; b) B. Purushothaman, S. R. Parkin, M. J. Kendrick, D. David, J. M. Ward, L. Yu, N. Stingelin, O. D. Jurchescu, O. Ostroverkhova, J. E. Anthony, *Chem. Commun.* **2012**, *48*, 8261–8263; c) J. Lee, M. J. Bruzek, N. J. Thompson, M. Y. Sfeir, J. E. Anthony, M. A. Baldo, *Adv. Mater.* **2013**, *25*, 1445–1448; d) M. J. Bruzek, J. E. Anthony, *Org. Lett.* **2014**, *16*, 3608–3610; e) M. M. Payne, S. R. Parkin, J. E. Anthony, *J. Am. Chem. Soc.* **2005**, *127*, 8028; f) B. Purushothaman, M. Bruzek, S. R. Parkin, A.-F. Miller, J. E. Anthony, *Angew. Chem. Int. Ed.* **2011**, *50*, 7013–7017; *Angew. Chem.* **2011**, *123*, 7151–7155.

[6] D. Chun, Y. Cheng, F. Wudl, *Angew. Chem. Int. Ed.* **2008**, *47*, 8380–8385; *Angew. Chem.* **2008**, *120*, 8508–8513.

[7] a) I. Kaur, W. Jia, R. P. Kopreski, S. Selvarasah, M. R. Dokmeci, C. Pramanik, N. E. McGruer, G. P. Miller, *J. Am. Chem. Soc.* **2008**, *130*, 16274–16286; b) I. Kaur, N. N. Stein, R. P. Kopreski, G. P. Miller, *J. Am. Chem. Soc.* **2009**, *131*, 3424–3425; c) I. Kaur, N. N. Stein, P. Prusevich, G. P. Miller, *J. Am. Chem. Soc.* **2010**, *132*, 1261–1263.

[8] for Reviews, see: a) U. H. F. Bunz, J. U. Engelhart, B. D. Lindner, M. Schaffroth, *Angew. Chem. Int. Ed.* **2013**, *52*, 3810–3821; *Angew. Chem.* **2013**, *125*, 3898–3910; b) U. H. F. Bunz, *Pure Appl. Chem.* **2010**, *82*, 953–968; c) U. H. F. Bunz, *Chem. Eur. J.* **2009**, *15*, 6780–6789; d) G. J. Richards, J. P. Hill, T. Mori, K. Ariga, *Org. Biomol. Chem.* **2011**, *9*, 5005–5017; for recent contributions on azahexacenes and azaheptacenes, see: e) B. D. Lindner, J. U. Engelhart, O. Tverskoy, A. L. Appleton, F. Rominger, A. Peters, H. J. Himmel, U. H. F. Bunz, *Angew. Chem. Int. Ed.* **2011**, *50*, 8588–8591; *Angew. Chem.* **2011**, *123*, 8747–8750; f) J. Engelhart, O. Tverskoy, U. H. F. Bunz, *J. Am. Chem. Soc.* **2014**, *136*, 15166–15169.

[9] T. M. Figueira-Duarte, K. Müllen, *Chem. Rev.* **2011**, *111*, 7260–7314.

[10] a) J. Xiao, C. D. Malliakas, Y. Liu, F. Zhou, G. Li, H. Su, M. G. Kanatzidis, F. Wudl, Q. Zhang, *Chem. Asian J.* **2012**, *7*, 672–675; b) J. Xiao, S. Liu, Y. Liu, L. Ji, X. Liu, H. Zhang, X. Sun, Q. Zhang, *Chem. Asian J.* **2012**, *7*, 561–564; c) H. M. Duong, M. Bendikov, D. Steiger, Q. Zhang, G. Sonmez, J. Yamada, F. Wudl, *Org. Lett.* **2003**, *5*, 4433–4436; d) J. Xiao, Y. Divayana, Q. Zhang, H. M. Doung, H. Zhang, F. Boey, X. W. Sun, F. Wudl, *J. Mater. Chem.* **2010**, *20*, 8167–8170.

[11] J. Xiao, H. M. Duong, Y. Liu, W. Shi, L. Ji, G. Li, S. Li, X.-W. Liu, J. Ma, F. Wudl, Q. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 6094–6098; *Angew. Chem.* **2012**, *124*, 6198–6202.

[12] a) A. Mateo-Alonso, *Chem. Soc. Rev.* **2014**, *43*, 6311–6324. For other peri-fused systems, see: b) Y. Fogel, M. Kastler, Z. Wang, D. Andrienko, G. J. Bodwell, K. Müllen, *J. Am. Chem. Soc.* **2007**, *129*, 11743–11749; c) L. Zhang, A. Fonari, Y. Liu, A.-L. M. Hoyt, H. Lee, D. Granger, S. Parkin, T. P. Russell, J. E. Anthony, J.-L. Bredas, V. Coropceanu, A. L. Briseno, *J. Am. Chem. Soc.* **2014**, *136*, 9248–9251.

[13] a) J. K. Stille, E. L. Mainen, *J. Polym. Sci. Part B* **1966**, *4*, 665–667; b) J. K. Stille, E. L. Mainen, *Macromolecules* **1968**, *1*, 36–42.

[14] B. Gao, M. Wang, Y. Cheng, L. Wang, X. Jing, F. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 8297–8306.

[15] Most interestingly, single-crystal X-ray data have only been reported for a few PFP derivatives to date: a) S. More, S. Choudhary, A. Higelin, I. Krossing, M. Melle-Franco, A. Mateo-Alonso, *Chem. Commun.* **2014**, *50*, 1976–1978; b) X. Feng, F. Iwanaga, J.-Y. Hu, H. Tomiyasu, M. Nakano, C. Redshaw, M. R. J. Elsegood, T. Yamato, *Org. Lett.* **2013**, *15*, 3594–3597 and Ref. [14]. However only two PFP structures (Ref. [15b]) and (Ref. [14]) show a packing of the molecules by π–π stacking.

[16] B. Kohl, F. Rominger, M. Mastalerz, *Org. Lett.* **2014**, *16*, 704–707.

[17] a) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322; b) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873; c) E. E. Nesterov, Z. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **2005**, *127*, 10083–10088; d) D. Zhao, T. M. Swager, *Macromolecules* **2005**, *38*, 9377–9384; e) T. M. Swager, *Acc. Chem. Res.* **2008**, *41*, 1181–1189.

[18] a) Y.-Z. Tan, B. Yang, K. Parvez, A. Narita, S. Osella, D. Beljonne, X. Feng, K. Müllen, *Nat. Commun.* **2013**, *4*, 2646; b) Q. Zhang, H. Peng, G. Zhang, Q. Lu, J. Chang, Y. Dong, X. Shi, J. Wie, *J. Am. Chem. Soc.* **2014**, *136*, 5057–5064.

[19] see for instance: R. Goddard, M. W. Haenel, W. C. Herndon, C. Krüger, M. Zander, *J. Am. Chem. Soc.* **1995**, *117*, 30–41.

[20] Oligoynes are also π-conjugated systems, which owing to their linear molecular shape often show a deviation from exact linearity of the sp-carbon chain in the solid state. See for instance: a) A. Lucotti, M. Tommasini, D. Fazzi, M. Del Zoppo, W. A. Chalifoux, M. J. Ferguson, G. Zerbi, R. R. Tykwinski, *J. Am. Chem. Soc.* **2009**, *131*, 4239–4244; b) S. Eisler, A. D. Slepkov, E. Elliott, T. Luu, R. McDonald, F. A. Hegmann, R. R. Tykwinski, *J. Am. Chem. Soc.* **2005**, *127*, 2666–2676.

[21] S. Ehrlich, H. F. Bettinger, S. Grimme, *Angew. Chem. Int. Ed.* **2013**, *52*, 10892–10895; *Angew. Chem.* **2013**, *125*, 11092–11096.

[22] For a large nonlinear starphene characterized by single-crystal X-ray diffraction, see: E. C. Rüdiger, M. Porz, M. Schaffroth, F. Rominger, U. H. F. Bunz, *Chem. Eur. J.* **2014**, *20*, 12725–12728.

[23] D. Wasserfallen, M. Kastlere, W. Pisula, W. A. Hofer, Y. Fogel, Z. Wang, K. Müllen, *J. Am. Chem. Soc.* **2006**, *128*, 1334 – 1339.
[24] program SADABS 2012/1 for absorption correction: G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin **2012**.
[25] program SHELXL-2014/7 (Sheldrick, 2014): G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

Received: December 12, 2014
Revised: March 4, 2015