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Saddle Shaped Hexaaryl[*a,c,fg,j,l,op*]-tetracenes from 4,5,9,10-Tetrafunctionalized Pyrenes

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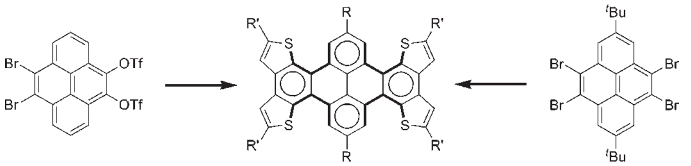
ABSTRACT



1: R = H; R' = *n*-Bu
2: R = *t*-Bu; R' = H

A new K-region functionalized pyrene is presented which was used as a building block for the straightforward synthesis of hexaaryl[*a,c,fg,j,l,op*]tetracene via fourfold Stille coupling and subsequent cyclodehydrogenation. Electronic properties and crystal structures are provided and reveal a saddle conformation for the curved hexaarylated tetracenes.[1]

Polycyclic aromatic hydrocarbons (PAHs) have been of major interest in research for many years due to their structural rigidity and variety, large π-system, strong π-stacking, and thereof derived application in printed electronics.[2−5] Consisting of four fused benzene rings, pyrene is the smallest *peri*-condensed PAH and its structural motif is a versatile platform for extended π-systems.[6−10] The specific extension of PAHs by penta- and benzannulation has been utilized to alter optical and electronic properties and can additionally lead to distortion. More precisely, PAH discs are forced out of planarity either by retention of the typical C−C distances in incorporated five-membered rings or by steric strain induced by atom crowding.[11−13] The synthesis of nonplanar PAHs is challenging and often suffers from low yields. Nevertheless, huge efforts have been made because curved structures are of special interest as model compounds for fullerenes and carbon nanotubes.[11,14,15] As examples for annulated and nonplanar pyrene derivatives, fourfold cyclopenta-fused pyrenes are reported to exhibit a bowl shape and tetrabenzo[*de,hi,mn,qr*]tetracene (old nomenclature: pyreno-(1′,2′:1,2)-pyrene) shows a high torsion of the tetracene backbone.[16,17] In the latter case, by benzannulation two *fjord*-regions are formed which are known as effective motifs for steric overcrowding of overlapping hydrogen atoms resulting in distortion.

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(1) The formally incorrect use of double bonds together with Clar sextets in the abstract figure has been made to indicate the stability arising from the dibenzo[*e,l*]pyrene.
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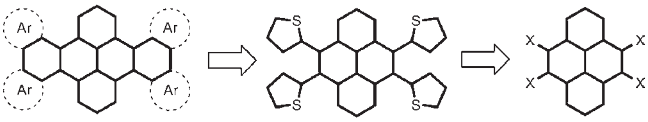
In our approach, we aimed to favor bending over twisting in order to pattern curved conjugated structures.[18] Therefore, we followed the concept of steric overcrowding and in particular chose a fourfold *fjord* arrangement (Scheme 1). Retrosynthetic considerations led to the need of a pyrene building block substituted with halogens at positions 4, 5, 9, and 10 for a palladium catalyzed cross-coupling reaction. The cyclodehydrogenation between outer aryl rings was identified as a crucial step due to the buildup of steric strain for molecular distortion. Thiophene was chosen because we reasoned that the cyclodehydrogenation reaction proceeds more smoothly between thiophenes than benzene rings and has already been reported on *ortho*-di(thien-2-yl)pyrenes.[10] Geometry optimization carried out on the core structure with the DFT-(B3LYP) method on the 6-31G level predicts a curved shape due to intramolecular repulsion between the lone pair electrons of sulfur atoms and hydrogen (Figure S14, Supporting Information (SI)).

Scheme 1. Retrosynthesis of a Fourfold *Fjord* Structure

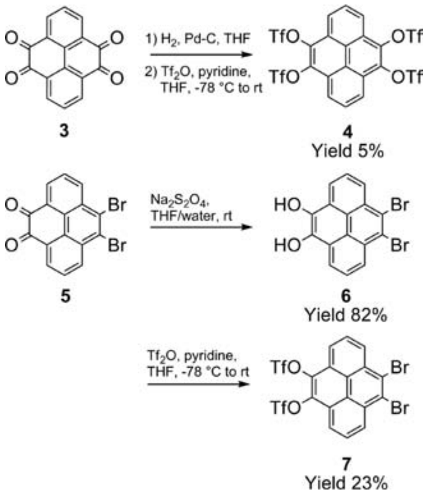


In the literature derivatization of pyrene at positions 4, 5, 9, and 10 is described either by ruthenium-catalyzed oxidation[19] or by bromination[20] of priorly *tert*-butylated pyrene in the presence of iron. *tert*-Butyl groups are known to heavily influence molecular packing and can easily form carbocations. To avoid these side effects we were searching for alternative methods to introduce aryl units in the K-region of pyrene without prior *tert*-butylation. The only reported synthesis of 4,5,9,10-tetraphenylpyrene has been accomplished in five steps starting from benzene derivatives and exemplifies the difficulty.[21]

Herein, we describe the synthesis and electronic and structural properties of hexaaryltetracenes **1** and **2**. A new building block applicable to palladium catalyzed reactions for pyrene related materials has therefore been developed.

Our first attempts were focused on the conversion of tetraketopyrene **3**[19] to tetratriflatopyrene **4** (Scheme 2). Unfortunately, yields turned out to be poor and the tetrahydroxy intermediate was not isolable. Expecting higher stability from a dihydroxy intermediate, we found that after reduction of **5** intermediate **6** could be isolated easily. The complete reduction of the diketone was proven in ^{1}H NMR experiments by the exchange of the alcohol proton to deuterium after D_2O addition. Further treatment of compound **6** with trifluoromethanesulfonic anhydride in the presence of pyridine gave **7** in 23% yield.

Scheme 2. Synthesis of Compounds **4** and **7**



Fourfold Stille coupling of **7** and **9**[20] with the corresponding tri-*n*-butyl(thiophen-2-yl)stannane gave 4,5,9,10-tetra(thien-2-yl)pyrenes **8** and **10** in moderate yields (Scheme 3). Subsequent ring closure to **1** could be achieved by treatment with iron(III) chloride, which is commonly applied in cyclodehydrogenation reactions.[22−24] We assume that the low yield of 17% is caused by the side reactions of the β-thienyl position with pyrene active sites 1, 3, 6, and 8. However, in the case of **10** iron(III) chloride could not be used due to free α-positions of the thienyl rings and polymerization as a side reaction. Instead, irradiation of **10** in the presence of iodine as an oxidant yielded hexaaryl-[*a*,*c*,*fg*,*j*,*l*,*op*]tetracene **2** via a light induced cyclization reaction in 60% yield.[25]

In order to investigate the influence of the cyclodehydrogenation between thiophenes on the optical and electronic properties, UV/vis absorption and cyclic voltammetry (CV) of compounds **8**, **1**, **10**, and **2** were performed (Figure 1). CV revealed only small changes in HOMO levels for thienyl and thieno derivatives. No reduction process was observed under the measurement conditions.

Judging by the onset of UV/vis absorption, a decrease of the optical band gap of 0.07 eV (**8** → **1**) and 0.11 eV (**10** → **2**) was determined. This bathochromic shift of the absorption is caused by the extension of the π-conjugated system as a result of the cyclodehydrogenation. The observed red shift of the emission onset from the opened to the fused species is in accordance with the absorption red shift. In comparison to the transition of the band gap from naphthalene to

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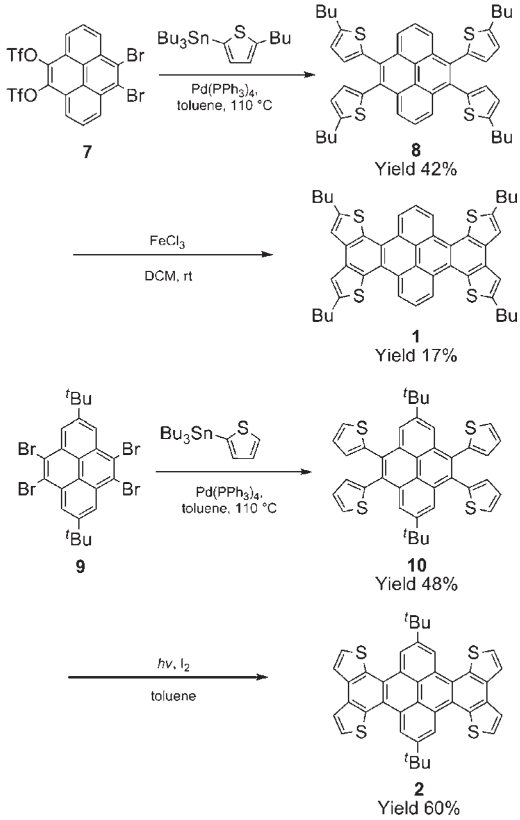
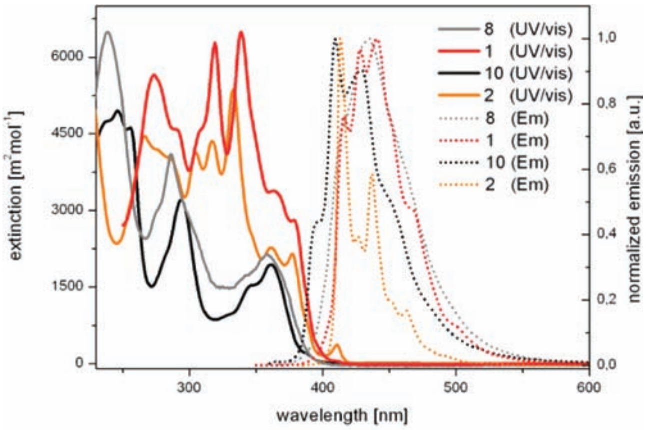
Scheme 3. 4,5,9,10-Tetrathienylation and Subsequent Oxidative Cyclodehydrogenation to Hexaaryl[*a,c,fg,j,l,op*]tetracenes **1** and **2**



tetracene, only a small change occurred in our system.[26] Following Clar's sextet rule, acene-like delocalization of π-electrons can obviously not be found for hexaaryl[*a,c,fg,j,l,op*]tetracenes **1** and **2**. Furthermore, the fusion between thiophenes increased the rigidity of the molecules, which is indicated by the pronounced vibronic structure characteristic of their UV/vis spectra.[10,24]

To prove the approach of curved structures via four *fjord*-regions, single crystals of compounds **1** and **2** were analyzed by X-ray diffraction. Figure 2 shows the ORTEP drawings of **1** and **2** in front and side views. As predicted by calculation (Figure S14, SI), both compounds exhibit a saddle conformation in which the pyrene ends and benzodithiophene units are curved oppositely. Within the bent structure, benzene rings A and B (see Figure 2f) show planarity and are used as reference planes for curvature survey. Rings A are similarly tilted against each other by 35.4° (**1**) and 36.0° (**2**), respectively. Angles of 26.2° (**1**) and 30.4° (**2**) were determined for rings B. The higher degree of distortion of compound **2** is most likely due to the steric demand of the *tert*-butyl groups. In addition, deviation from planarity influences the bond length. C–C Distances within rings A and B range from 1.39 to 1.44 Å, whereas 1.46 to 1.47 Å were found for the bonds between rings A and B and 1.45 Å between B and B. As expected, the C–C bond length within rings A and B match with common distances in isolated benzene rings which is in accordance to Clar's sextet rule. Furthermore it should be emphasized that annulated "acenes" mainly exhibit a twist in contrast to



	λ_{abs}[a]/nm	λ_{em}[b]/nm (λ_{ex})[c]/nm	λ_{edge}/nm	$E_{g(opt)}$[d]/eV	$E_{HOMO(CV)}$[e]/ eV
8	359	435 (358)	389	3.19	-5.53
1	378	416 (339)	397	3.12	-5.34
10	361	396 (350)	383	3.24	-5.56
2	377	413 (340)	396	3.13	-5.54

Figure 1. Extinction and emission spectra of compounds **1**, **2**, **8**, and **10** in THF.[a] λ_{abs} is the absorption band appearing at the longest wavelength.[b] λ_{em} is the fluorescence band appearing at the shortest wavelength.[c] λ_{ex} wavelength of excitation.[d] Calculated from λ_{edge}.[e] CV measured in 0.1 M *n*-Bu_4NPF_6/DCM with a scan rate of 100 mV s^{-1}; values calculated using the ferrocene HOMO level: $E_{HOMO(CV)} = -(E_{ox,onset} - E^{(1/2)}{}_{Fc/Fc+} + 4.8)$ eV.

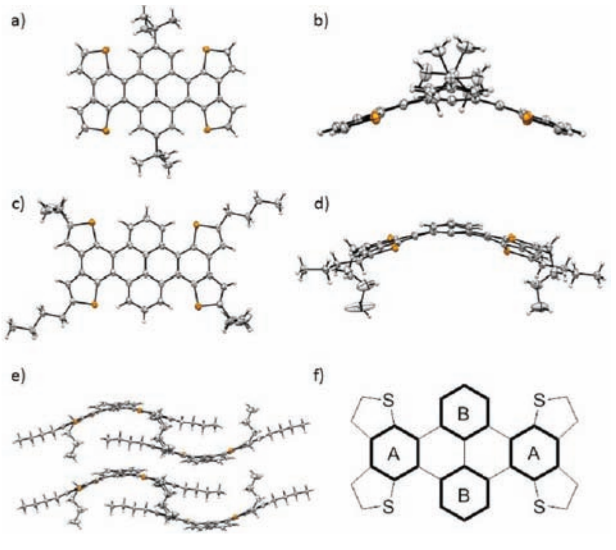


Figure 2. X-ray structure of **1** and **2**. Two of four *n*-butyl side chains are disordered. For clarity, only the majority component is shown. (a) **2** front view; (b) **2** side view; (c) **1** front view; (d) **1** side view; (e) crystal packing of **1**; (f) illustration of planar benzene rings A and B; used for calculation of curving angles.

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the here found bent shape within the "acene" backbone, which is ascribed to the unique rim of hexaarylated tetracenes.[13]

Crystal packing of **1** and **2** is depicted in Figures 2e, S15 and S16 (SI), respectively. For **1**, brick-like order was found in which the benzodithiophene units are located above each other with an A–A′ distance of 3.45 to 3.75 Å. This overlap is enabled by the flexibility of *n*-butyl chains which alternate from angled to an all-*trans* conformation. Arrangement in the crystal of *tert*-butylated hexaaryltetracene **2** is dominated by the bulky side groups, and molecules stack around THF filled channels.

In summary, curved hexaaryl[*a,c,fg,j,l,op*]tetracenes have been synthesized via Pd-catalyzed cross-coupling reactions in the K-region and subsequent cyclodehydrogenation. To avoid prior *tert*-butylation of pyrene, a versatile building block was invented which allowed closer packing of the hexaaryltetracene. X-ray analysis revealed a saddle conformation due to a high accumulation of *fjord*-regions which induced a bent vs a twisted structure.

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Supporting Information Available. Full experimental procedures and characterization data. CIF files from the X-ray analysis of **1**, **2**, **4**, **7**, and **8** - CCDC 830178, 830176, 830174, 830175, and 830177. This material is available free of charge via the Internet at http://pubs.acs.org.