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Synthesis and Aggregates of Phenylene−Ethynylene Substituted Polycyclic Aromatic Compounds

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Introduction. Conjugated polymers and oligomers are of significant interest due to their optical, electrical, and electrooptical properties that lead to applications in various electronic devices as well as sensors. However, defects in the polymeric backbone have a remarkable effect on the device efficiency and sometimes lead to irreproducible device performance. Oligomers can be obtained defect free and synthesized with tunable, well-defined molecular weights. The well-defined nature of the oligomers facilitates also the control over their supramolecular structure, crucial for the realization of optimal molecular devices.[1] Therefore, oligomers serve not only as models for the corresponding polymers but can be used in many applications as active materials. Additionally, the molecules can be end-capped with (different) terminal groups that alter their optoelectronic as well as structure forming properties. For example, in the case of phenylene−ethynylene oligomers, donor/acceptor substituted molecules have been shown to exhibit interesting optical properties.[2] Thioacetyl- and thiocarbamoyl end-capped phenylene−ethynylenes were investigated by AFM methods.[3] To keep the synthetic effort for the preparation of the defined structures feasible, small structures such as dimers, trimers, etc., serve as key structures for the investigation of the corresponding structure−property relationship in oligomers (and polymers). For example, derivatives of 1,4-bis(phenylethynyl)benzene are widely used as models for the investigation of the electron transport properties of phenylene−ethynylenes.[4]

During our studies on polycyclic aromatic hydrocarbons (PAHs) we became interested in the incorporation of these structural motifs in defined shape-persistent linear and cyclic molecules.[5] The use of PAHs as active materials in electronic and electrooptical devices is an area of dynamic research.[6] However, most reports about all-benzenoic PAHs deal either with highly substituted or with unsubstituted materials;[7] the synthesis of mono- or difunctionalized PAHs has been only sparingly investigated.[8] Therefore, large PAHs as functional parts of more complex molecular architectures (e.g., in the center or as end groups) can only be rarely found.[9] In particular, we are not aware of any studies on the inclusion of dibenzonaphthacenes in complex molecular architectures. Here we report the synthesis of monofunctionalized dibenzonaphthacenes and their sulfur analogues. We show that these building blocks can be introduced as end groups in defined molecular architectures by the use of transition-metal-catalyzed C−C coupling reactions. Besides the synthesis of these new materials, we will describe the aggregation of the compounds in solution as well as their structures on a solid substrate.

Results and Discussion. The synthesis of the polycyclic aromatic compounds is outlined in Scheme 1. Details of the synthesis as well as the characterization of all compounds are given in the Supporting Information (SI).

The key step in our synthesis is the combination of the transformation of dihalo 2,4,6-triarylpyrylium salts (**1**) to dihalo 1,2,3,5-tetraarylbenzenes by condensation with the corresponding sodium aryl acetates and their subsequent Pd(0)-catalyzed dehydrohalogenation.[11] As

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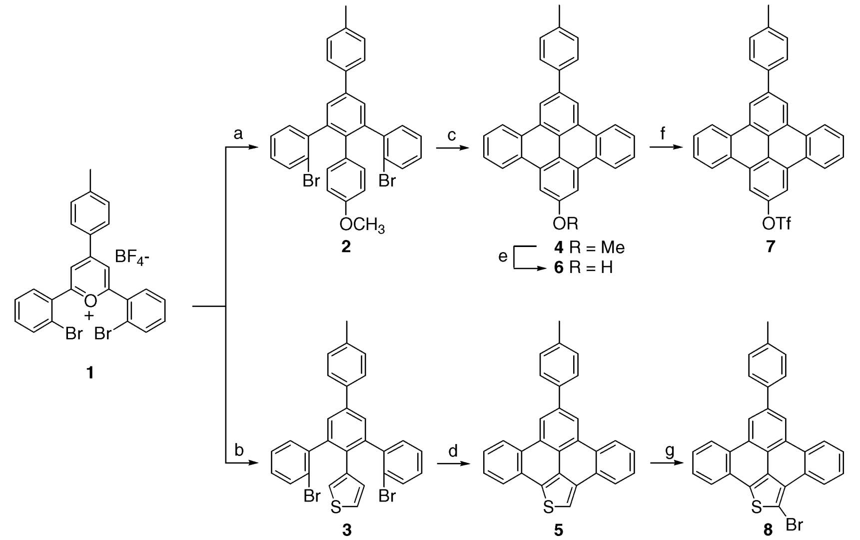
Scheme 1. Synthesis of Monofunctionalized Polycyclic Aromatics[a]



[a] (a) Sodium 4-methoxyphenylacetate, Ac_2O, 37%; (b) sodium 3-thienylacetate, Ac_2O, 46%; (c) $PdCl_2(PPh_3)_2$, DBU, 42%; (d) $PdCl_2(PPh_3)_2$, DBU, 28%; (e) BBr_3, 96%; (f) Tf_2O, pyridine, 68%; (g) NBS, 97%.

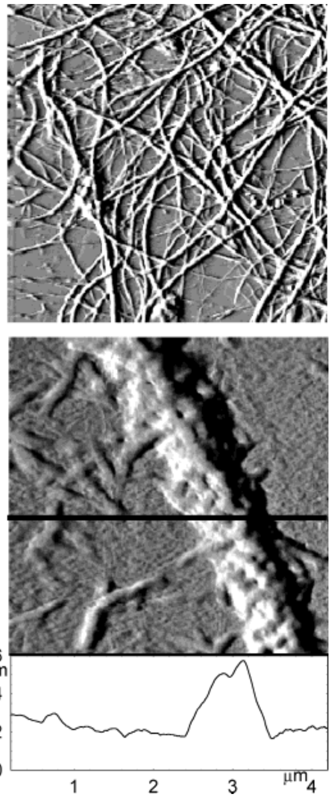


Figure 1. Error signal AFM images (noncontact mode) of **16** on mica cast from THF/*n*-octane: (top) image size 10 × 10 *µ*m; (middle) image size 4 × 4 *µ*m; (bottom) topographical profile along the black line in the image above.

we have shown earlier, the metal-catalyzed "double-barrel" cyclization of appropriate precursors gives the corresponding dibenzonaphthacenes in good to acceptable yields when the initially formed Pd(II) species attacks an electron-rich aryl ring. This is the anisyl ring in **2** and the thienyl ring in **3**.[5] Both polycyclic aromatics (**4** and **5**) can be transformed into monofunctionalized compounds capable of undergoing transition-metal-catalyzed C−C coupling reactions. **4** was demethylated with BBr_3 to give the phenol **6** and transformed into the triflate **7** by treating with Tf_2O. **5** has only one reactive position at the electron-rich part of the molecule and gives after treating with NBS cleanly the monobromo compound **8**.

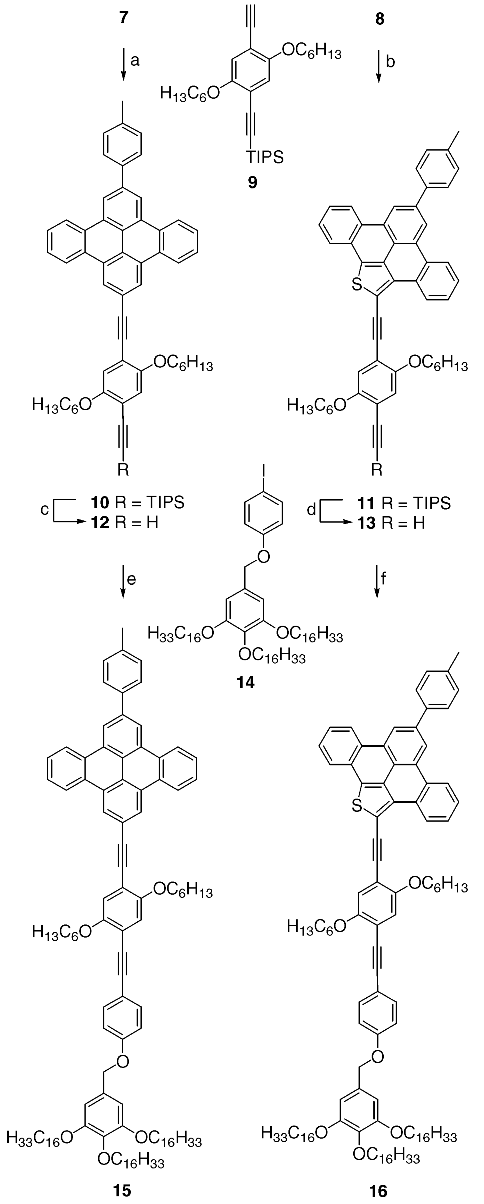
Aromatic bromides and triflates are widely used as substrates in transition-metal-catalyzed C−C coupling reactions and allow the introduction of these aromatics in more complex molecular architectures as described in Scheme 2.

Pd-catalyzed coupling with **9**[12] in the presence of CuI afforded **10** and **11** which after deprotection of the triisopropylsilyl group with tetrabutylammonium fluoride in THF yielded the phenylene ethynylenes **12** and **13**. Coupling with **14** gave **15** and **16** which both contain trialkoxybenzyl ethers as solubilizing end groups. Side products that arose from the oxidative homocoupling of the acetylenes are insoluble in all common solvents and could be easily removed by filtration.[13] On the contrary, all phenylene−ethynylene derivatives containing one terminal polycyclic aromatic moiety are soluble in aromatic and halogenated solvents as well as in THF. In some solvents the NMR signals of the compounds are concentration-dependent, an indication for the aggregation tendency of the condensed aromatic part of the structures. Under the assumption that the monomer−dimer equilibrium is the predominant process in solution, the aggregation constant for **16** in CH_2Cl_2 was determined by concentration-dependent NMR spectroscopy to be 20 M^{-1}.[14]

AFM Characterization of Solution Grown Superstructures. Solutions of **16** were dip cast onto a freshly cleaved mica surface from THF, THF/*n*-octane, and THF/*n*-hexane mixtures. After complete evaporation of the solvent, the morphology of the dry samples was investigated by atomic force microscopy (AFM). It is reported that the thin film morphology and the structure of the supramolecular organization for oligo(phenylene−ethynylenes) are strongly solvent dependent.[3b] This was also found for **16**. From THF only a granular morphology of the material was observed (see SI). From THF/*n*-octane mixtures different superstructures could be identified on the substrate (Figure 1).

The molecules self-assemble into ribbons of different length, a width of several hundred nanometers (200−400 nm) and a height (mostly) between 20 and 50 nm

Scheme 2. Synthesis of 15 and 16[a]



[a] (a) $Pd(PPh_3)_4$, CuI, 68%; (b) $Pd(PPh_3)_4$, CuI, 64%; (c) Bu_4NF, 92%; (d) Bu_4NF, 87%; (e) $Pd(PPh_3)_4$, CuI, 60%; (f) $Pd(PPh_3)_4$, CuI, 63%.

(Figure 1, top). This shows that the cross section of the ribbons is not molecular, but an aggregation of several molecules occurs. Similar thin film morphologies are also found for other phenylene−ethynylenes. Also in those cases the cross section of the superstructures can be either molecular (for larger oligomers)[3a] or an aggregation of several molecules occurs.[3b] In some cases we could observe that ribbons with a width of 200−300 nm and a height of 5−15 nm aggregate into bundles that can reach nearly micrometer dimensions in diameter (Figure 1, middle). However, films cast from THF/*n*-hexane show a completely different morphology. The AFM images resemble polymer single crystals and indicate that the molecules can form highly ordered superstructures when deposited from solution (Figure 2).[15]

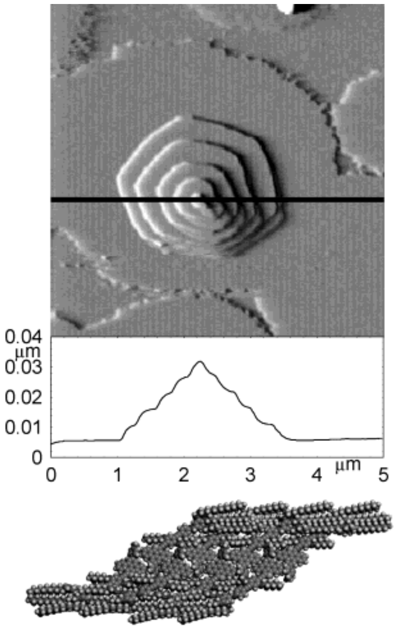


Figure 2. Error signal AFM images (contact mode) of **16** on mica cast from THF/*n*-hexane: (top) image size 5 × 5 µm; (middle) topographical profile along the black line in the image above; (bottom) molecular double layers have a height of approximately 5 nm.

They form structures with a diameter of several microns, a hexagonal base, and relatively sharp boundaries, resembling Babylonian ziggurats.[16] The number of the equidistant steps of about 5 nm determines their height, ranging from 15 to 30 nm. In some cases (lower right part of the ziggurat in Figure 2), also layers with a thickness of approximately 3 nm could be identified, similar to the plateau height on which the ziggurats are located. It is also worth mentioning that the plateau on mica has fuzzy boundaries and does not show a symmetrical shape. As far as we know, this morphology has not been observed before for phenylene−ethynylenes. At present, we attribute this difference to the strong aggregation tendency of the polycyclic aromatic part of the nonsymmetric molecules together with their uniform size. Under the assumption that the ends of the molecule tend to phase separate, the height of the ziggurats can be explained with the adsorption of double layers as shown in Figure 2, bottom. Accordingly, layer heights of around 3 nm could be a result of the adsorption of monolayers. Ongoing investigations deal with the influence of the molecule length on the film morphology as well as possible applications of these materials in molecular electronics.

Conclusion. Polycyclic aromatics capable of undergoing CC coupling reactions are synthesized in a two-step route starting from the corresponding pyrylium salts. Since the latter are available with a variety of substitution patterns, condensed aromatics with different degrees and positions of the reactive groups are available. These compounds can be used as building blocks for complex molecular architectures, in this case phenylene−ethynylenes. These compounds aggregate in solution as determined by concentration-dependent NMR experiments. Additionally, on a solid substrate different superstructures could be identified. Among these are not only ribbon-like but also ziggurate-like structures, indicating the formation of a highly ordered arrangement of the molecules on the mica surface.

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Supporting Information Available: Experimental details, synthetic procedures, and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) We acknowledge the hint by one of the referees that the term “ziggurat” describes the structures in Figure 2 more accurately than the term “pyramid”.

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