Organic & Supramolecular Chemistry

Synthesis of Dumbbell-Like DBATT Dimers**

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Two-dimensional acenes are promising candidates for applications in single-molecule spectroscopy due to the electronic properties caused by their zig-zag periphery. However, synthetic access to their dimers remains unexplored because of low solubility and reduced stability. Herein we report a facile approach towards two-dimensional acenes dimers on the example of 2.3,8.9-dibenzanthanthrene (**DBATT**) connected via rigid linker. The exploitation of dehydrative π-extension on the last step of the synthesis allows avoiding difficulties connected with cumbersome purification of low soluble products. The technique was shown to be applicable for the synthesis of **DBATT** dimers connected rigidly with conjugated and non-conjugated linkers, containing alternating para-phenylene and bicyclo[2.2.2]octane moieties.

Investigations on the potential applications of large polycyclic aromatic compounds (PAHs) have emerged as a dominant part of material science in 21 century.[1–3] The renaissance of carbon nanostructures was inevitable because physical properties can be easily tuned via the size, shape, and edge topology[4] of the molecules, but was delayed by the development of methods of organic chemistry and physical methods. Recent progress in techniques of C—C bond formation allowed the precise synthesis of various carbon-based nanostructures[5–10] and in-

creased sensitivity and abundance of NMR (nuclear magnetic resonance), HRMS (high-resolution mass spectrometry), and HPLC (high-performance liquid chromatography) analyses granted possibility to ease and fast check of purity of the compounds.

Edge topology of PAHs directly influences the electronic and optical properties of the compounds. For example, NGs containing zig-zag edges exhibit strong absorption in the visible region, because of the low HOMO − LUMO gap (where HOMO represents highest occupied molecular orbital and LUMO represents lowest unoccupied molecular orbital). Reduced HOMO − LUMO gap allows designing semiconductors with high carrier mobilities,[11–13] materials for non-linear optics[14] and molecular spintronics.[15]

But like everything in this world, advantages do not come without disadvantages. Zig-zag periphery is very reactive, and linear acenes immediately polymerize and oxidize in solutions.[16] Meanwhile, by changing the linear annulation mode of acenes to an angular one can significantly improve their stability. However, to achieve absorption in 500–700 nm increased amount of carbons is required, which vastly decreases the solubility. Modification of two-dimensional acenes with bulky substituents[17–21] can solve this problem, but in some applications, it is inappropriate. One of the examples is the study of coherent dipole-dipole coupling,[22] where 2.3,8.9-dibenzanthanthrene (**DBATT**) was found as a candidate for the single-molecule optical transistor.[23] During the investigations of these phenomena, it was found, that the statistical distribution of **DBATT** molecules is not appropriate for the stable reproducibility of the experiments because it is difficult to find two molecules in the same state and environment.

Hypothetically, this problem can be solved by connecting two **DBATT** molecules with a rigid non-conjugated linker (Scheme 1). Synthesis of chromophore dimers is typical in the investigations blue emitters,[24] charge transfer,[25–27] and singlet fission.[28–31] Nevertheless, to our knowledge, the synthesis of higher two-dimensional acenes is not described in the literature.

Herein, we show the approach to dumbbell-like **DBATT** dimers connected via rigid linkers for potential applications in single-molecule spectroscopy.

Precise post-modification of large PAHs is a huge challenge in organic chemistry because of the reasonable amount of reaction centers in the molecules and their low solubility.[32] **DBATT** is no exception in this respect, and its easy oxidation complicates the task even further. Suzuki reaction is one of the most convenient reactions for the C—C bond formation in

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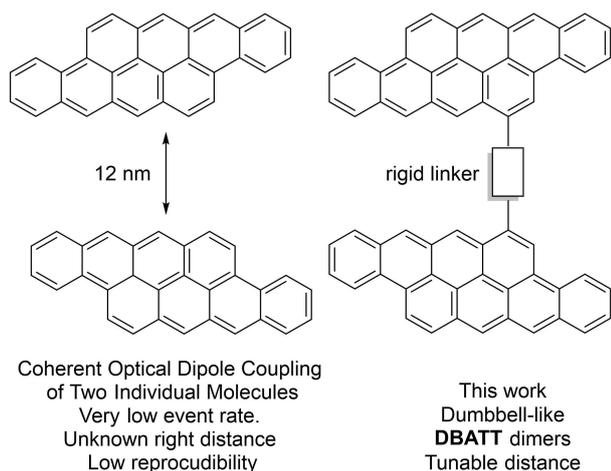Nikolaus-Fiebiger Str. 10, 91058 Erlangen,
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Scheme 1. Justification of this work.

Scheme 2. Selection of building block. NBS: N-Bromosuccinimide.

aromatic derivatives.[33] As a requirement, C–Hal (Hal=Cl, Br, I) and a boronate moiety have to be present in the respective precursors. None of the known methods can selectively functionalize **DBATT** molecule, and low solubility of products hampers the possibility of their separation.

Recently, we have reported a very successful approach to the synthesis of two-dimensional acenes and its homologs. A new method, called DPEX (a dehydrative π-extension) acid-promoted reductive intramolecular cyclization of the aromatic aldehydes is the core stage of the approach.[34–37] One of the described features was the tolerance of reaction conditions to the presence of bromines in the structure. However, the synthetic utility of brominated **DBATT**s in the Suzuki reaction was low due to the formation of a mixture of oxidation side products and mono/bis adducts.

Nevertheless, the utilization of the precursor of brominated **DBATT** (**1**) can solve the mentioned problems with separation and specific functionalization (Scheme 2). To confirm this assumption, we started the synthesis of dumbbell dimers from the borylation of commercially available 4,4''-dibromo-p-terphenyl **4**, which *para*-terphenylene core was used as a model linear rigid linker (Scheme 3). Suzuki reaction of **6** with **1** resulted in 23% yield, and product **8** was exposed to standard DPEX reaction conditions. **DBATT** dimer **10** was isolated in 75%. The extremely low solubility of **10** prevented the registration of ^{1}H NMR even at elevated temperatures, so the formation of the product and its purity were confirmed via combination of high-temperature HPLC and HRMS analyses (see Supporting Information).

Between known non-conjugated hydrocarbons, which can mimic benzene moiety, bicyclo[2.2.2]octane (**BCO**)[38] was chosen as the most promising candidate for decoupling of π-systems of **DBATT** fragments. 1,4-Di-(4-bromophenyl)bicyclo [2.2.2]octane, an analogue of **4** was synthesized according to the literature procedure.[39] Following the established procedure, **DBATT** dimer **11** was successfully synthesized with 64% on the last step.
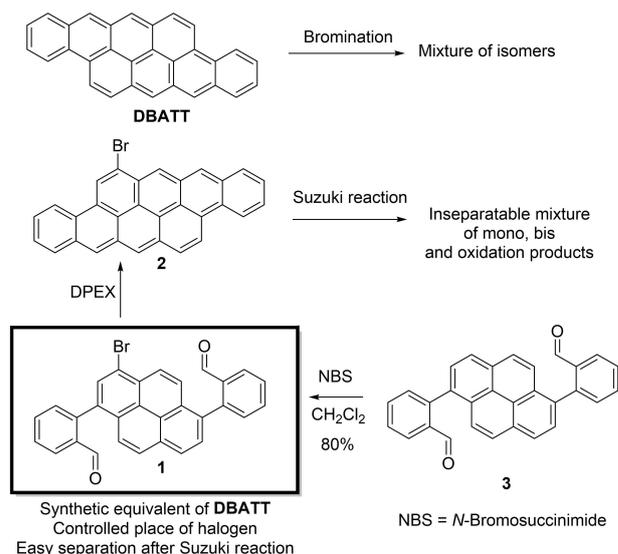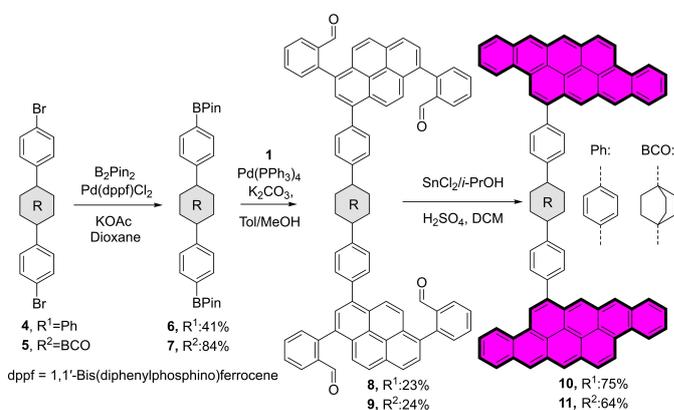
Scheme 3. Synthesis of dumbbell-like **DBATT** dimers.

Comparison of UV spectra of pristine **DBATT**, **10**, and **11** are depicted in Figure 1. Blueshift is observed when the rigid linker
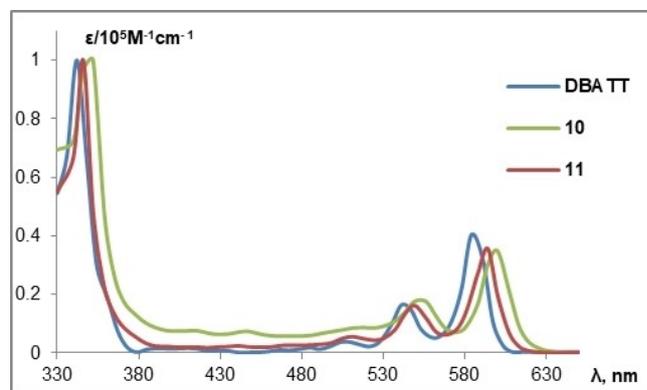

Figure 1. Comparison of UV-Vis spectra of pristine DBATT and DBATT dimers 10 and 11 in 1,2-Dichlorobenzene at 298 K.

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is switched from **4** to **5**, indicating the presence of additional conjugation between the **DBATT** fragments in **10**. Redshift between in **11** compared to pristine **DBATT** can be explained via the influence of extra phenyl ring in the aromatic system.

In conclusion, we developed new synthetic approach towards dumbbell-like **DBATT** dimers connected with rigid linkers. The synthesis is based on the exploitation of **DBATT** synthetic equivalent, which allows the forming of labile chromophore core in the last step of the synthesis and avoids cumbersome purification. The tuning of size and amount of bicyclo [2.2.2]octane fragments is virtually possible. The research of coherent dipole-dipole interactions is currently in progress.

Supporting Information summary.

Details of the synthetic procedures, copies of NMR, mass, UV − Vis, HPLC chromatograms.

Conflict of Interest

The authors declare no conflict of interest.

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