## Boron-Doped Tri(9,10-anthrylene)s: Synthesis, Structural Characterization, and Optoelectronic Properties

### Claas Hoffend, Frauke Schödel, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner<sup>\*[a]</sup>

Abstract: The reaction of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (9,10-dibromo-DBA, 3) with two equivalents of 9-lithio-2,6- or 9-lithio-2,7-di-tert-butylanthracene gave the corresponding 9,10-dianthryl-DBAs featuring two (4) or four (5) inwardpointing tert-butyl groups. Compound 4 exists as two atropisomers, 4 and 4', due to hindered rotation about the exocyclic B-C bonds. X-ray crystallography of 5 suggests that the overall interactions between facing tert-butyl groups are attractive rather than repulsive. Even in solution, 4/4' and 5 are stable toward air and moisture for several hours. Treatment of 3 with 10lithio-9-R-2,7-di-tert-butylanthracenes carrying phenyl (R=Ph), dimesitylboryl ( $R = Mes_2B$ ), or N,N-di(p-tolyl)ami-

#### no $(R = Tol_2N)$ groups gave the corresponding 9,10-dianthryl-DBA derivatives 9-11 in moderate to good yields. In these molecules, all four solubilizing tert-butyl groups are outward pointing. The solid-state structures of 4, 5, 9, and 10 reveal twisted conformations about the exocyclic B-C bonds with dihedral angles of 70-90°. A significant electron-withdrawing character was proven for the Mes<sub>2</sub>B moiety, but no appreciable + M effect was evident for $Tol_2N$ . Compounds 5, 9, and 11 show two reversible DBA-centered reduction waves in the cyclic voltammogram. In

**Keywords:** boranes • charge transfer • conjugation • electrochemistry • luminescence the case of 10, a third reversible redox transition can be assigned to the Mes<sub>2</sub>B-anthryl substituents. The UV/ Vis absorption spectrum of 5 is characterized by a very broad band at  $\lambda_{max} =$ 510 nm, attributable to a twisted intramolecular charge-transfer interaction from the anthryl donors to the DBA acceptor. The corresponding emission band shows pronounced positive solvatochromism  $(\lambda_{\rm em} = 567 \, \rm nm,$  $C_6H_{12};$  $680 \text{ nm}, \text{ CH}_2\text{Cl}_2$ ) in line with a highly polar excited state. The charge-transfer bands of 10 and 11, as well as the emission bands of 9 and 10, are redshifted relative to those of 5. The Tol<sub>2</sub>N derivative 11 is essentially nonfluorescent in solution, but emits bright wine-red light in the solid state.

### Introduction

Boron-containing conjugated  $\pi$ -electron systems are enjoying increasing attention because of their outstanding optoelectronic properties,<sup>[1-6]</sup> which find applications, for example, in new conducting and semiconducting polymers for plastic electronics<sup>[7]</sup> or in anion sensor technology.<sup>[8]</sup>

In recent years, 9,10-dihydro-9,10-diboraanthracene (DBA) derivatives **A** (Figure 1) were recognized for the following reasons as versatile building blocks of boron-doped organic materials. 1) Their rigid framework guarantees optimal  $\pi$  overlap between the boron atoms and the 1,2-phenylene bridges. Appropriately designed **A**-type compounds are therefore highly luminescent and/or behave as reversible

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Figure 1. Symmetrically ( $R^1 = R^2 = H$ , halogen, OR, NR<sub>2</sub>, alkyl, aryl, vinyl) and unsymmetrically ( $R^1 = Mes$ ,  $R^2 = H$ , Br, OR, vinyl; Mes = mesityl) substituted 9,10-dihydro-9,10-diboraanthracenes **A**; stabilization of **A** by structural constraint as exemplified in **B**; protection of the vacant boron-centered p orbitals in **C** by mesityl groups; 9,10-dianthryl-9,10-dihydro-9,10-diboraanthracenes **D** and their structural relationship with **C**.

two-step redox systems.<sup>[6,9–13]</sup> 2) Its cyclic structure renders the DBA skeleton more stable than comparable open-chain derivatives.<sup>[13,14]</sup> 3) The proximity of the two boron atoms leads to binding cooperativity (e.g., the ditopic Lewis base

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pyridazine binds more strongly than two equivalents of pyridine).<sup>[15,16]</sup> Given this background, a variety of symmetrically  $(R^1=R^2=H,^{[9]} halogen,^{[13,17-20]} OR,^{[13]} NR_2,^{[19]} alkyl,^{[21,22]} aryl,^{[12,14,23]} vinyl;^{[9]} Figure 1) and unsymmetrically (R<sup>1</sup>=Mes, R<sup>2</sup>=H, Br, OR, vinyl; Mes=mesityl)<sup>[13]</sup> substituted DBAs have been synthesized and thoroughly characterized.$ 

However, a serious problem often encountered with compounds A lies in the sensitivity of their exocyclic  $B-R^{1,2}$ bonds toward air and moisture. Kinetic stabilization of DBA derivatives has so far been achieved either by structural constraint or by the introduction of steric bulk. In the first case, the tetracoordinate intermediate preceding hydrolytic decomposition is destabilized by embedding the boron atoms into a rigidly fixed planar framework (see **B**; Figure 1).<sup>[14]</sup> In the second case, mesityl substituents ( $R^1 = R^2 = Mes$ ) are introduced into the molecule so that the vacant boron-centered p orbitals are protected from the top and bottom by methyl groups (see C; Figure 1).<sup>[12]</sup> Solutions of 9,10-dimesityl-9,10-dihydro-9,10-diboraanthracene (C) are stable for extended periods of time even in nondried solvents and under an ambient atmosphere (NMR spectroscopic control). Unfortunately, the compound offers only a limited degree of tunability.

In the search for alternative substituents, which combine a level of steric protection similar to that of the mesityl group with a larger number of set-screws for manipulating the optoelectronic properties of the corresponding DBA derivative, 9-anthryl moieties appear particularly attractive. 1) H-C1 and H-C8 in **D** (Figure 1) serve a similar purpose to the ortho-methyl groups in C. 2) 9-Anthryl substituents contain an extended  $\pi$ -electron system; many of them are therefore both luminescent and redox active. 3) The 10-position of the 9-anthryl group is well-suited for further functionalization  $(\mathbf{R}^3)$ , either with the aim of influencing its electronic properties or to prepare oligomers  $[-\{B(\mu-C_6H_4)_2B\}-(9,10-anthra$ cenediyl)–]<sub>n</sub>. 4) For steric reasons, the DBA and 9-anthryl planes in **D** should be orthogonal to each other. Pronounced charge-transfer interactions can be anticipated between both fragments if the HOMO levels of the 9-anthryl moieties and the LUMO level of the DBA core are appropriately adjusted.

Any system in which two chromophores are linked by a single bond possesses, in the perpendicular conformation, several twisted intramolecular charge-transfer (TICT) states, which may give rise to unique optoelectronic properties.<sup>[24-26]</sup> Because the radiative back transition from the TICT state to the ground state is overlap forbidden, many TICT states are nonluminescent and therefore lead to intramolecular fluorescence quenching. However, by coupling to suitable vibrations this transition can gain intensity from more allowed states,<sup>[24]</sup> which explains the appreciable TICT fluorescence quantum yields of various compounds like, for example, oligo(9,10-anthrylene)s.<sup>[27-35]</sup>

Herein, we report on the synthesis and structural characterization of compounds **D** carrying electronically innocent (i.e., Ph), potentially  $\pi$ -accepting (i.e., Mes<sub>2</sub>B), and  $\pi$ -donating (i.e., Tol<sub>2</sub>N; Tol=*p*-tolyl) substituents R<sup>3</sup>. These compounds can be regarded as boron-doped analogues of tri(9,10-anthrylene)s and a comparison of the optoelectronic properties of the two classes of compounds will therefore be revealing.

#### **Results and Discussion**

In a first series of exploratory experiments, we treated 9,10dibromo-DBA (**A**;  $\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{Br}$ )<sup>[13]</sup> with two equivalents of 9-lithioanthracene<sup>[36]</sup> in diethyl ether and obtained a brickred microcrystalline solid, which was insoluble in all common solvents. We therefore decided to introduce solubilizing side chains into the 9-anthryl substituents and selected the readily available 2,6-di-*tert*-butyl derivative for further investigations.

Synthesis of soluble 9,10-dianthryl-9,10-dihydro-9,10-diboraanthracenes: Friedel-Crafts alkylation of anthracene with tBuCl/AlCl<sub>3</sub> in CHCl<sub>3</sub> provided a 3:2 mixture of the literature-known isomers 2,6- and 2,7-di-tert-butylanthracene.<sup>[37]</sup> The products were conveniently separated by selective extraction of the 2,7-isomer into acetone (see the Supporting Information). Treatment of 2,6-di-tert-butylanthracene with N-bromosuccinimide/FeCl<sub>3</sub> in CHCl<sub>3</sub> gave 1 (Scheme 1) in excellent yield.[33] Lithium-bromine exchange on compound 1 with *n*BuLi, followed by the addition of 9,10-dibromo-DBA (3; Scheme 1) led to the formation of the 9,10-dianthryl-DBAs 4 and 4' (Scheme 1). The deep-red compounds 4 and 4' are soluble in  $C_6H_6$ , toluene, THF, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>, can be purified by flash column chromatography on silica gel under an ambient atmosphere, and are stable in nondried C<sub>6</sub>D<sub>6</sub> for several hours (NMR spectroscopic control; first signs of decomposition are detectable after approximately 6 h).

Compounds 4 and 4' are rotamers, which arise from impeded rotation about the exocyclic B–C bonds. The <sup>11</sup>B{<sup>1</sup>H} NMR resonances of 4 and 4' are broadened beyond detection. In the <sup>1</sup>H NMR spectrum, 4 and 4' give rise to two sets of signals with overall integral ratios of 4:5. Even though we succeeded in growing single crystals of 4 (see below), separation of the two rotamers on a preparative scale was not possible. Thus, we cannot unambiguously assign a specific signal set to either 4 or 4'. Similar rotamers have previously been reported for a 4-type tri(9,10-anthrylene), in which the DBA core is replaced by 2,6-di-*tert*-butyl-anthracene-9,10-diyl and for which the sterically less congested atropisomer corresponding to 4' is preferentially formed and has been structurally characterized.<sup>[33]</sup>

The X-ray crystal structure analysis of **4** fully confirms its proposed molecular structure (Figure 2; Table 1). In the solid state, the molecule possesses  $C_s$  symmetry. The length of the exocyclic bond B1–C1 (1.577(7) Å) is essentially the same as in 9,10-dimesityl-DBA (1.589(2) Å<sup>[12]</sup>). The 9-anthryl substituent in **4** and the plane spanned by C31, B1, and C34 are orthogonal (dihedral angle = 88.9(1)°) and the two symmetry-related 9-anthryl moieties are nearly coplanar to

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Scheme 1. Synthesis of compounds 4/4' and 5. Reagents and conditions: i) *n*BuLi (3 equiv), Et<sub>2</sub>O,  $-78^{\circ}C \rightarrow$  room temperature, 1 h; ii) Et<sub>2</sub>O/toluene,  $-78^{\circ}C \rightarrow$  room temperature, 12 h.

Table 1. Crystallographic data for 4 and 5.

	4	5
formula	C <sub>56</sub> H <sub>58</sub> B <sub>2</sub>	$C_{56}H_{58}B_2 \times C_6H_6$
$M_{ m r}$	752.64	830.75
color, shape	red, plate	red, block
<i>T</i> [K]	173(2)	173(2)
radiation, $\lambda$ [Å]	Mo <sub>Kα</sub> , 0.71073	Mo <sub>Kα</sub> , 0.71073
crystal system	orthorhombic	orthorhombic
space group	$Cmc2_1$	Pccn
a [Å]	29.405(3)	22.9053(16)
b [Å]	9.1756(10)	24.3415(13)
c [Å]	16.6838(16)	9.2511(7)
α [°]	90	90
β[°]	90	90
γ[°]	90	90
V [Å <sup>3</sup> ]	4501.4(8)	5157.9(6)
Ζ	4	4
$ ho_{ m calcd}  [ m g  cm^{-3}]$	1.111	1.070
F(000)	1616	1784
$\mu \text{ [mm}^{-1}\text{]}$	0.062	0.059
crystal size [mm <sup>3</sup> ]	$0.24 \times 0.24 \times 0.13$	$0.25 \times 0.24 \times 0.19$
reflns collected	10352	32634
independent reflns $(R_{int})$	2231 (0.1186)	4553 (0.0813)
data/restraints/parameters	2231/1/262	4553/9/276
GOF on $F^2$	0.959	1.018
$R_1, wR_2 [I > 2\sigma(I)]$	0.0603, 0.1027	0.0956, 0.2004
$R_1, wR_2$ (all data)	0.0930, 0.1118	0.1296, 0.2190
largest diff. peak and hole $[e Å^{-3}]$	0.164, -0.171	0.319, -0.260

each other (dihedral angle= $2.3(1)^\circ$ ). This conformation results in a close approach of the two *tert*-butyl substituents at C23 and C23A (shortest distance between two carbon atoms: C10 $\cdots$ C10A=4.455(11) Å; shortest H $\cdots$ H contacts:

3.6–3.9 Å). Despite this steric interaction, the two *tert*-butyl groups do not seem to have a pronounced tendency to avoid each other because the DBA core in **4** is only slightly distorted from planarity (dihedral angle between the two *ortho*-phenylene rings =  $169.2(3)^{\circ}$ ).

Given the structural features of 4, the question arises of how far the limits of steric demand around the DBA center can be pushed and whether the molecule is able to accommodate four inward-pointing tert-butyl substituents. To synthesize the corresponding molecule 5 (Scheme 1), 2,7-di-tert-butylanthracene was first brominated selectively at its 9-position by applying the same conditions as in the case of the 2,6-derivative (see the Supporting Information). The resulting compound 2 was lithiated and the lithio anthracene species was reacted with 3 to obtain 5 in 86% yield.

Compared to **4** and **4'**, **5** shows a similarly good solubility and even enhanced stability toward air and moisture.

The <sup>1</sup>H NMR spectrum of **5** is characterized by one signal at  $\delta = 1.24$  ppm (integrating 36H) for the four *t*Bu groups, two multiplets at  $\delta = 6.72$  (4H) and 7.62 ppm (4H) for the DBA core, and four signals for the 9-anthryl moieties. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is also in full agreement with the proposed highly symmetric molecular structure. In the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum, **5** gives rise to an extremely broad signal at  $\delta = 73$  ppm.

X-ray crystallography of 5 (Figure 2; Table 1) reveals a  $C_i$ symmetric framework with a planar DBA core. In contrast to 4, the plane of the anthryl group in 5 is inclined by an angle of 72.4(2)° relative to the DBA plane. However, the two anthryl substituents remain coplanar, with the shortest C…C (H…H) distances between facing substituents being 3.876(7) Å (2.7-3.0 Å). We also note that the increased steric interaction in 5 does not lead to an elongation of its exocyclic B1-C1 bonds (1.576(5) Å) as compared to 4 (1.577(7) Å). This observation, together with the fact that the facing tert-butyl groups could easily avoid each other if the two anthryl planes were inclined in opposite directions, suggests that the tBu...tBu interaction in 5 is not entirely repulsive but, on the contrary, that dispersion forces are causing a stabilizing attraction. In this context, we refer to hexakis(3,5-di-tert-butylphenyl)ethane, in which the tert-butyl groups stabilize the compound relative to its dissociation product radicals by as much as 40 kcalmol<sup>-1</sup> through attractive dispersion interactions.<sup>[38]</sup> Here, the shortest tBu-tBu



Figure 2. Molecular structures of **4** (top) and **5** (bottom) in the solid state; displacement ellipsoids are drawn at the 50% probability level, H atoms have been omitted for clarity. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]: **4**: B1–C1 1.577(7), B1–C31 1.559(7), B1–C34 1.562(7); C1-B1-C31 120.2(4), C1-B1-C34 120.9(4), C31-B1-C34 118.8(4); Ar(C31)//Ar(C34) 169.2(3), Ant(C1)//C31B1C34 88.9(1), Ant(C1)//Ant(C1A) 2.3(1); **5**: B1–C1 1.576(5), B1–C31 1.553(5), B1–C36A 1.567(5); C1-B1-C31 120.9(3), C1-B1-C36A 119.8(3), C31-B1-C36A 119.3(3); Ar(C31)//Ar(C36A) 0.0, Ant(C1)//C31B1C36A 72.4(2), Ant(C1)//Ant(C1A) 0.0. Ar=phenylene, Ant=anthryl. Symmetry transformations used to generate equivalent atoms: A: -x, y, z (**4**); -x+1, -y+1, -z+1 (**5**).

distances amount to about 4.05 Å (C…C) and 2.5 Å  $(H\dots H)$ .<sup>[39]</sup>

Tuning the electronic properties of 9,10-dianthryl-9,10-dihydro-9,10-diboraanthracenes: Having explored key steric issues of 9,10-dianthryl-DBAs, we now focus on electronic substituent effects. Compound 1 was abandoned from further studies to circumvent problems of rotamer formation in the final DBA products (see 4, 4'). Our synthetic efforts therefore relied on compound 2 and on the replacement of its bromine atom by electron-donating or -withdrawing substituents. The selection of these substituents had to take into account the fact that the overall synthetic sequence requires a second bromination reaction (at the 10-position of the anthracene molecule) with which they needed to be compatible. The phenyl, dimesitylboryl (Mes<sub>2</sub>B), and N,N-di-(p-tolyl)amino (Tol<sub>2</sub>N) groups turned out to be suitable substituents, which, moreover, cover a broad range of different electronic properties (see 6-8; Scheme 2). Compounds 6-8 were prepared from 2 through Suzuki coupling with PhB(OH)<sub>2</sub>, lithiation/treatment with Mes<sub>2</sub>BF, and Buchwald-Hartwig coupling with Tol<sub>2</sub>NH, respectively, followed by bromination with N-bromosuccinimide/FeCl<sub>3</sub> (see the Supporting Information). The same general protocols as in the cases of 4/4' and 5 were applied to subsequently prepare the 9,10-dianthryl-DBAs 9-11 from 6-8 (Scheme 2). We wish to emphasize that the synthetic sequence applied necessarily leads to anthryl DBA derivatives in which all four tert-butyl groups are outward pointing. We also note that 10 can not only be viewed as a 9,10-dianthryl-DBA, but also as a molecule featuring two 9,10-diborylated anthracene chromophores. Related quadrupolar compounds of the general formula  $Mes_2B-(\pi system)-BMes_2$  have been thoroughly studied by Marder et al. and reported to possess interesting linear and nonlinear optical properties.[40]

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As already noted for 4/4', no <sup>11</sup>B NMR resonances were detectable for 9-11. For a discussion of key aspects of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **9–11**, it is first helpful to closely examine the NMR parameters of the anthracene precursors 9-R-2,7-di-tert-butylanthracene (9-R-2,7-DTBA; R = Ph,  $Mes_2B$ ,  $Tol_2N$ ). NMR spectroscopy provides essential information on the electron density distribution within  $\pi$ -conjugated molecules. Because proton shifts are strongly influenced by solvent and magnetic anisotropy effects, <sup>13</sup>C shifts are generally preferred for the determination of local  $\pi$ -charge densities.<sup>[41]</sup> Compared to 9-Ph-2,7-DTBA, the <sup>13</sup>C nuclei 8a, 9a, and 10 in 9-Mes<sub>2</sub>B-2,7-DTBA, which are located ortho and para to the boryl group (black circles in compound 10; Scheme 2), are deshielded by approximately  $\Delta \delta = 3-4$  ppm, whereas the *meta*-carbon resonances (i.e., 4a, 10a) of both compounds possess essentially the same shift values ( $\Delta \delta = 0.2$  ppm). As anticipated, this indicates a certain degree of  $\pi$  conjugation between the anthracene unit and the boron atom. In contrast to a priori expectations, the <sup>13</sup>C NMR parameters of the atoms 8a/9a and 10 reveal only negligible differences between 9-Ph-2,7-DTBA and 9-Tol<sub>2</sub>N-2,7-DTBA ( $\Delta \delta = 0.1$  and 0.3 ppm, respectively). Moreover, the <sup>13</sup>C nucleus 9 of 9-Tol<sub>2</sub>N-2,7-DTBA is far less deshielded  $(\delta = 137.5 \text{ ppm})$  than the *ipso*-<sup>13</sup>C nuclei of the *para*-tolyl rings ( $\delta = 146.1$  ppm); the *para*-tolyl rings also show strongly shielded *ortho*-<sup>13</sup>C nuclei ( $\delta$ =120.5 ppm). It may therefore be concluded that the  $\pi$ -donor capacity of the nitrogen atom is essentially restricted to the para-tolyl groups. The fact that the Mes<sub>2</sub>B group exerts a measurable -M effect on the anthracene  $\pi$  system, whereas the Tol<sub>2</sub>N substituent does not appear to have any appreciable +M effect, may be explained by assuming an (on average) stronger twist about

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Table 2). Due to the small crystal size, the data obtained for 10 were poor. We therefore refrain from a detailed discussion of its structural parameters. Compound 9 crystallizes with two crystallographically independent molecules  $(9_A \text{ and } 9_B)$ in the asymmetric unit. Compounds  $9_A/9_B$  possess a center of inversion and the tert-butyl substituents are pointing away from the DBA core. Nevertheless, their exocyclic B1-C1 bond lengths (1.589(4))1.581(4) Å) are the same as in the seemingly more crowded derivatives 4 (1.577(7) Å) and 5 (1.576(5) Å), which lends further support to the conclusion that the inward-pointing tertbutyl groups do not repel each other. The DBA moieties in  $9_A/$  $9_{\rm B}$  are planar and form dihedral angles with the anthryl substituents of 81.6(2)/88.5(1)°.

Electrochemical measurements on 9.10-dianthryl-9.10-dihydro-

9,10-diboraanthracenes: Com-

pounds 4/4', 5, and 9-11 were

investigated by cyclic voltam-

Scheme 2. Synthesis of compounds **9–11**. Reagents and conditions: i) 1) *n*BuLi (3 equiv), Et<sub>2</sub>O,  $-78^{\circ}C \rightarrow room$  temperature, 1 h; 2) **3** (1 equiv), Et<sub>2</sub>O/toluene,  $-78^{\circ}C \rightarrow room$  temperature, 12 h. Black circles in **10**: <sup>13</sup>C nuclei experiencing deshielding upon going from 9-Ph-2,7-DTBA to 9-Mes<sub>2</sub>B-2,7-DTBA; white circles in **10**: <sup>13</sup>C nuclei experiencing deshielding upon going from 9-Mes<sub>2</sub>B-2,7-DTBA to **10**.

the Tol<sub>2</sub>N–C(anthryl) bond than the Mes<sub>2</sub>B–C-(anthryl) bond. Indeed, the solid-state structure of 9-Tol<sub>2</sub>N-2,7-DTBA (9-Mes<sub>2</sub>B-2,7-DTBA) shows a dihedral angle of 65.9° (54.4°) between anthracene and the plane spanned by the two remaining *ipso*carbon atoms and the nitrogen (boron) atom (see the Supporting Information and ref. [40a] for the related X-ray crystal structure analysis of 9,10-bis-(dimesitylboryl)anthracene).

After the introduction of the anthryl substituents into the DBA scaffold, changes in certain <sup>13</sup>C NMR shift values are apparent in all three cases, which are qualitatively and quantitatively comparable to the changes observed upon going from 9-Ph-2,7-DTBA to 9-Mes<sub>2</sub>B-2,7-DTBA: the <sup>13</sup>C nuclei *ortho* to the DBA boron atom experience downfield shifts of about  $\Delta \delta = 3$  ppm (i.e., 4a, 10a; white circles in compound **10**; Scheme 2), whereas the resonances of the *meta*-<sup>13</sup>C nuclei (i.e., 8a, 9a) remain unchanged ( $\Delta \delta \le 0.5$  ppm). The three DBA <sup>13</sup>C NMR resonances vary by a maximum of  $\Delta \delta =$ 0.3 ppm between **9**, **10**, and **11**.

Compounds **9** and **10** have been structurally characterized by X-ray crystallography (Figure 3, Table 2. Crystallographic data for 9 and 10.

	9	10
formula	C68H66B2×1.5CH2Cl2	$C_{92}H_{100}B_4$
$M_{ m r}$	1032.22	1248.96
color, shape	red, block	red, plate
<i>T</i> [K]	173(2)	173(2)
radiation, $\lambda$ [Å]	Mo <sub>Kα</sub> , 0.71073	Mo <sub>Kα</sub> , 0.71073
crystal system	monoclinic	monoclinic
space group	$P2_{1}/c$	$P2_{1}/c$
a [Å]	25.5984(13)	17.579(4)
b [Å]	10.1849(4)	9.1886(15)
c [Å]	25.5600(12)	24.659(5)
α [°]	90	90
β[°]	118.775(3)	94.244(18)
γ [°]	90	90
V [Å <sup>3</sup> ]	5841.0(5)	3972.2(14)
Ζ	4	2
$ ho_{ m calcd}  [ m gcm^{-3}]$	1.174	1.044
F(000)	2188	1344
$\mu \text{ [mm^{-1}]}$	0.198	0.058
crystal size [mm <sup>3</sup> ]	$0.41 \times 0.36 \times 0.33$	$0.18 \times 0.16 \times 0.02$
reflns collected	67 536	24853
independent reflns $(R_{int})$	10758 (0.0810)	6978 (0.4522)
data/restraints/parameters	10758/0/681	6978/18/439
GOF on $F^2$	0.981	0.836
$R_1, wR_2 [I > 2\sigma(I)]$	0.0710, 0.1928	0.1198, 0.2481
$R_1$ , $wR_2$ (all data)	0.0975, 0.2098	0.3272, 0.3469
largest diff. peak and hole $[e Å^{-3}]$	0.723, -0.708	0.718, -0.319

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Figure 3. Molecular structures of  $9_A$  (top) and 10 (bottom) in the solid state; displacement ellipsoids are drawn at the 50% probability level, H atoms have been omitted for clarity. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]:  $9_A$ : B1–C1 1.589(4), B1–C31 1.551(4), B1–C36A 1.570(4); C1-B1-C31 121.5(2), C1-B1-C36A 119.4(2), C31-B1-C36A 119.0(2); Ar(C31)//Ar(C36A) 0.0, Ant(C1)//C31B1C36A 81.6(2), Ant(C1)//Ant(C1A) 0.0, Ant(C2)//Ph(C41) 66.6(1). Ar=phenylene, Ant=anthryl. Symmetry transformation used to generate equivalent atoms: A: -x+1, -y+1, -z+1.

metry (CV; THF,  $[nBu_4N][PF_6]$ , versus ferrocene/ferrocenium (FcH/FcH<sup>+</sup>)). Because the redox potentials recorded for the rotamer mixture 4/4' are the same as those of 5, only the cyclic voltammograms of compounds 5 and 9–11 will be discussed further (Table 3; Figure 4).

The assignment of individual redox waves is based on the comparison with 1) 9,10-dimesityl-DBA (C; Figure 1) as a prototypical DBA derivative with redox-innocent boron

Table 3. Electrochemical and UV/Vis data of 5 and 9-11.

	$\mathrm{CV}^{\mathrm{[a]}}$ $E_{_{1/2}}$ [V] vs. FcH/FcH+	Absorption <sup>[c]</sup> $\lambda_{\max} [nm] (\varepsilon [mol^{-1}dm^3 cm^{-1}])$	Fluorescence <sup>[c]</sup> $\lambda_{em}$ [nm] ( $\lambda_{ex}$ [nm])
5	$-1.73, -2.57, -3.21^{[b]}$	366 (15500), 510 (1050)	610 (366)
9	$-1.68, -2.46, -3.32^{[b]}$	374 (28200), 531 (1500)	635 (374)
10	$-1.70, -2.37, -2.64, -3.11^{[b]}$	346 (17400), 442 (18300), 536 (2000)	644 (442)
11	$-1.69, -2.42, -3.27^{[b]}, -3.39^{[b]}$	359 (20300), 429 (14300), 556 (2200)	675 (593) <sup>[d]</sup>

[a] THF, supporting electrolyte:  $[nBu_4N][PF_6]$  (0.1 m), scan rate: 200 mVs<sup>-1</sup>, versus FcH/FcH<sup>+</sup>. [b] Cathodic peak potential  $E_{pc}$  value. [c] C<sub>6</sub>H<sub>6</sub>. [d] Solid-state measurement.

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substituents and 2) anthracene and the corresponding 9-R-2,7-DTBAs (R=H, Ph, Mes<sub>2</sub>B, and Tol<sub>2</sub>N).

Under the measurement conditions applied throughout this study, compound **C** gives rise to two reversible redox waves at  $E_{\frac{1}{2}} = -1.84$  and -2.73 V;<sup>[42]</sup> the parent anthracene shows a first reversible reduction wave at  $E_{\frac{1}{2}} = -2.16$  V and an irreversible electron transition at  $E_{pc} =$ -2.55 V (THF, Na[BPh<sub>4</sub>], vs. FcH/FcH<sup>+</sup>).<sup>[32]</sup>

The cyclic voltammogram of 5 is characterized by two reversible redox waves at  $E_{1/2} = -1.73$ and -2.57 V. Moreover, an additional ill-defined feature appears at approximately  $E_{pc} =$ -3.21 V. Compound 9-H-2,7-DTBA shows two redox transitions at  $E_{1/2} = -2.65$  and  $E_{pc} =$ -3.24 V (see the Supporting Information for a CV-plot overlay of 9-H-2,7-DTBA, C, and 5). Given these data, the first reduction of **5** at  $E_{1/2} = -1.73 \text{ V}$ clearly occurs at the DBA fragment. An assignment of the second reduction at  $E_{i_{h}} =$ -2.57 V as either DBA- or anthryl-centered is less straightforward, but was finally achieved by means of UV/Vis spectroelectrochemistry. The UV/ Vis spectra of Li[A] and  $Li_2[A]$  $(R^1 = R^2 = H)$  in THF are litera-

of Li<sub>2</sub>[**A**] shows an absorption at  $\lambda_{max} = 420 \text{ nm}$  and a much weaker, broader band at  $\lambda_{max} = 500 \text{ nm}$  (Figure 5, top).<sup>[11]</sup> During exhaustive coulometric one-electron reduction of 9-H-2,7-DTBA, in situ UV/Vis spectroscopy (THF, [*n*Bu<sub>4</sub>N]-[PF<sub>6</sub>]) revealed a set of four broad bands emerging at  $\lambda_{max} = 550$ , 600, 690, and 740 nm (Figure 5, middle). For a comparative study on **5**, we took a solution in THF, added a small piece of elemental potassium

ture-known. Above 400 nm, Li[A] possesses the most in-

tense absorption at  $\lambda_{max} = 517$  nm, together with three broad

humps at  $\lambda_{\text{max}} = 730$ , 810, and 910 nm; the UV/Vis spectrum

piece of elemental potassium, and again performed in situ UV/Vis spectroscopy. First, the signature of a DBA monoanion developed in the spectrum ( $\lambda_{max}$ =535, 750, 830, 930 nm;

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Figure 4. Cyclic voltammograms of 5, 9, 10, and 11 as solutions in THF at room temperature; supporting electrolyte:  $[nBu_4N][PF_6]$  (0.1 M); scan rate: 200 mVs<sup>-1</sup>, versus FcH/FcH<sup>+</sup>.

Figure 5, bottom); after some time, these characteristic bands vanished and absorptions at  $\lambda_{\text{max}} = 474$  and 620 nm appeared instead (Figure 5, bottom). From the comparison of the spectra compiled in Figure 5, we thus tentatively assign the  $E_{\frac{1}{2}} = -2.57$  V wave of **5** to a DBA-centered reduction. In turn, the electron transition at  $E_{\text{pc}} = -3.21$  V is most likely associated with the anthryl substituents. One explanation for the surprising selectivity of the second DBA reduction over a first anthryl reduction might be that the +I



Figure 5. UV/Vis absorption spectra of Li[A] and Li<sub>2</sub>[A] (top;  $R^1=R^2=H$ ), of the 9-H-2,7-DTBA monoanion (middle), and of K[5] and K<sub>2</sub>[5] (bottom) in THF.

effect of the boron atom on the anthryl substituent outweighs its -M effect so that the redox potential of the anthryl fragment in **5** is shifted to more cathodic values than suggested by the model system 9-H-2,7-DTBA.

The cyclic voltammogram of 9 is similar to that of 5 and the two most anodic, reversible transitions appear at essentially the same potential values. Thus, neither the relocation of the *tert*-butyl groups nor the introduction of the two phenyl rings has an appreciable influence on the electrochemical properties of the molecules (see the Supporting Information for a CV-plot overlay of 9-Ph-2,7-DTBA, C, and 9).

This situation changes when the phenyl rings are replaced by Mes<sub>2</sub>B groups. As in the cases of **5** and **9**, compound **10** features reversible redox waves at  $E_{i/_2} = -1.70$  and -2.64 V; however, a third reversible transition is now visible at an intermediate electrode potential of  $E_{i/_2} = -2.37$  V. A fourth wave is found at  $E_{pc} = -3.11$  V. In comparison, the cyclic voltammogram of 9-Mes<sub>2</sub>B-2,7-DTBA is characterized by reduction events at  $E_{pc} = -2.46$  and -3.00 V (see the Supporting Information for a CV-plot overlay of 9-Mes<sub>2</sub>B-2,7-DTBA, C, and 10). Coulometric measurements on 10 provided clear evidence that the first (DBA-centered) reduction is a one-electron transition. When the potentiostat was set to a value between the second and third redox waves, two more electrons were transferred; coulometry at a slightly more cathodic potential value than the third redox wave led to an overall electron count of four. Spectroelectrochemical measurements carried out at an intermediate electrode potential between those of the second and third redox waves indicated the formation of both DBA dianions and anthryl monoanions. We therefore conclude that the second reduction of the DBA core and the first reduction of the anthryl substituents cannot be selectively achieved in the case of 10. A sizeable -M effect of the Mes<sub>2</sub>B groups on the anthryl  $\pi$  systems is therefore not only evident from the <sup>13</sup>C{<sup>1</sup>H} NMR spectra (see above), but also from the electrochemical studies.

The cyclic voltammogram of **11** reveals two reversible waves at  $E_{\frac{1}{2}} = -1.69$  and -2.42 V. Moreover, we observe two features at  $E_{pc} = -3.27$  and -3.39 V. Two electron transitions are visible in the voltammogram of 9-Tol<sub>2</sub>N-2,7-DTBA with associated redox potentials of  $E_{\frac{1}{2}} = -2.62$  and  $E_{pc} = -3.47$  V, largely identical to those of 9-H-2,7-DTBA. Thus, in line with <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, the Tol<sub>2</sub>N group does not seem to exert a notable +M effect on the anthryl scaffold, because this should result in a cathodic shift of the reduction potential relative to 9-H-2,7-DTBA. Although the first electron transition of **11** is again DBAcentered, the assignment of the second wave is less clear and might well have contributions from both DBA and anthryl moieties.

Electronic spectra of 9,10-dianthryl-9,10-dihydro-9,10-diboraanthracenes: The UV/Vis and fluorescence spectra of the rotamer mixture 4/4' are essentially identical to those of 5 and therefore are not considered further. We start our discussion with a comparison of the electronic spectra of 5 with those of its constituent chromophores, that is, 9-H-2,7-DTBA and C (solutions in  $C_6H_6$ ). The UV/Vis spectrum of 9-H-2,7-DTBA shows a longest-wavelength absorption band with vibrational fine structure at  $\lambda_{max} = 357 \text{ nm}$ . The corresponding band of C appears at  $\lambda_{max}\!=\!349\,\text{nm}$  and bears a shoulder on the bathochromic side. According to time-dependent DFT calculations, the strong absorption can be attributed to  $\pi$ - $\pi$ \* excitations of the DBA core, whereas the shoulder is due to intramolecular charge transfer from the electron-rich mesityl groups to the electron-poor DBA unit.<sup>[12]</sup> This observation already lends support to our concept to achieve TICT in DBA derivatives by extending the electron  $\pi$  system of the boron substituents. In line with that, the UV/Vis spectrum of 5 is characterized by two absorptions: one at  $\lambda_{max} = 366$  nm, which has a similar line shape to the 9-H-2,7-DTBA band and thus most likely arises from electron transitions within the anthryl  $\pi$  system, and the second at about  $\lambda_{max} = 510 \text{ nm}$ , which is broad and featureless and therefore assigned to an anthryl $\rightarrow$ DBA charge-transfer transition (Figure 6, Table 3; see the Sup-



Figure 6. UV/Vis absorption (top) and emission (bottom) spectra of DBA derivatives in  $C_6H_6$ ; 5 (red), 9 (black), 10 (green), 11 (blue).

porting Information for an overlay of the electronic spectra of 9-H-2,7-DTBA, C, and 5). Thus, upon going from mesityl to anthryl substituents, the charge-transfer band experiences a bathochromic shift of more than 100 nm. The fluorescence spectrum of 9-H-2,7-DTBA reveals a structured emission band at  $\lambda_{em} = 417$  nm ( $\lambda_{ex} = 358$  nm). Compound C also gives rise to a structured emission band at 413 nm in cyclohexane  $(C_6H_{12})^{[12]}$  and 460 nm in  $C_6H_6$  ( $\lambda_{ex}=350$  nm), but only one broad band is visible in THF, at  $\lambda_{em} = 483 \text{ nm.}^{[12]}$  The pronounced redshift with increasing solvent polarity suggests that the emissive state of C is highly polarized and already has contributions from TICT emission. The associated quantum yields are small ( $\phi_f = 0.02 - 0.05$ );<sup>[12]</sup> however, given the pronounced vibrational fine structure generally observed for absorption and emission bands of anthracene derivatives, a switch from mesityl (see C) to anthryl (see 5 and 9-11) should have a beneficial effect on the quantum yields obtained (see the Introduction).

In contrast to 9-H-2,7-DTBA and **C**, the emission band of **5** is bathochromically shifted and appears at  $\lambda_{em} = 610$  nm when the molecule is excited at either  $\lambda_{ex} = 366$  nm (anthryl absorption) or  $\lambda_{ex} = 510$  nm (charge-transfer band; Figure 6, Table 3). The absorption spectrum of **5** is largely solvent-independent, but the fluorescence spectrum exhibits pronounced positive solvatochromism, that is, the emission

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Figure 7. Solvatochromism of **5** in solvents of different polarity ( $C_6H_{12}$ ,  $C_6H_6$ , THF,  $CH_2Cl_2$ ); UV/Vis absorption (top) and emission (bottom) spectra.

band is redshifted in more polar solvents:  $\lambda_{em} = 565$  (C<sub>6</sub>H<sub>12</sub>), 610 (C<sub>6</sub>H<sub>6</sub>), 660 (THF), 680 nm (CH<sub>2</sub>Cl<sub>2</sub>; Figure 7). Characteristically, in the least polar solvent, C<sub>6</sub>H<sub>12</sub>, both the chargetransfer band and the fluorescence band of **5** gain a vibrational fine structure.

The UV/Vis and fluorescence spectra of **9** in  $C_6H_6$  are similar to those of **5** with all key bands being shifted bathochromically by 8–25 nm (Figure 6, Table 3; see the Supporting Information for an overlay of the electronic spectra of 9-Ph-2,7-DTBA, **C**, and **9**).

In the UV/Vis spectra of 10 and 11 ( $C_6H_6$ ), two strong absorptions (instead of one in the cases of 5 and 9) appear at  $\lambda_{\text{max}} = 346, 442 \text{ nm}$  (10) and  $\lambda_{\text{max}} = 359, 429 \text{ nm}$  (11). Similar features are visible in the UV/Vis spectra of 9-Mes<sub>2</sub>B-2,7-DTBA and 9-Tol<sub>2</sub>N-2,7-DTBA, so these two bands are most likely substituent-centered. In addition, we also observe charge-transfer bands at  $\lambda_{max} = 536$  and 556 nm for 10 and 11, respectively (Figure 6, Table 3). The Mes<sub>2</sub>B derivative 10 also shows an emission at  $\lambda_{em} = 644 \text{ nm}$  ( $\lambda_{ex} = 442 \text{ nm}$ ), whereas no appreciable fluorescence of 11 is detectable in  $C_6H_6$ . In contrast to the solution state, solid 11 shows a wine-red emission at  $\lambda_{em} = 675 \text{ nm}$  ( $\lambda_{ex} = 593 \text{ nm}$ ; see the Supporting Information for an overlay of the electronic spectra of 9-Mes<sub>2</sub>B-2,7-DTBA/9-Tol<sub>2</sub>N-2,7-DTBA, C, and 10/11). An elucidation of the reasons for the differences in the solution and solid-state fluorescence of 11 certainly requires more detailed scrutiny. A reasonable working hypothesis would be that restricted rotation in the solid state reduces nonradiative decay pathways operative in solution, a phenomenon known as aggregation-induced emission.<sup>[43]</sup>

In summary, we find the following trend in the chargetransfer bands of 9–11:  $\lambda_{max} = 531$  (9)  $\approx 536$  (10) < 556 nm (11). Compounds 9 and 10 show essentially identical behavior even though 10 is equipped with  $\pi$ -electron-withdrawing Mes<sub>2</sub>B substituents, because the effect of the boryl group is most pronounced for the anthryl LUMO,<sup>[5]</sup> whereas the charge transfer proceeds from the anthryl HOMO into the DBA LUMO. The presence of  $\pi$ -electron-donating Tol<sub>2</sub>N substituents in 11 increases the HOMO levels of the corresponding anthryl moieties,<sup>[44]</sup> which explains why 11 shows the most redshifted charge-transfer band. However, the shift is small compared to 9 and 10, in line with our previous conclusions that the nitrogen atom uses most of its  $\pi$ -donor capacity toward the *p*-tolyl rings rather than its anthryl substituent.

With regard to the fluorescence spectra, we note that all DBA derivatives gave rise to an additional emission at around  $\lambda_{em} = 440$  nm upon irradiation into the respective anthryl absorption band. When the samples were prepared in a glovebox with rigorously dried and degassed solvents, the intensity of this band was very small (approximately 5% of the intensity of the main band), but it could never be completely suppressed. The 440 nm emission gained in intensity if the closed cuvette was left standing for extended periods of time outside the glovebox or if air and moisture were deliberately admitted. Thus, a certain sensitivity of 5 and 9-11 toward hydrolysis and/or oxidation is apparent from fluorescence spectroscopy, even though the compounds can be purified under ambient atmosphere by column chromatography (5 and 9) or extraction with nondried MeOH (10 and 11). As already stated above, targeted hydrolysis studies, monitored by NMR spectroscopy, gave signs of decomposition not earlier than 6 h after the addition of H<sub>2</sub>O.<sup>[45]</sup>

In C<sub>6</sub>H<sub>6</sub>, **5**, **9**, and **10** gave quantum yields  $\phi_f$  of 0.08, 0.05, and 0.06, respectively. In contrast, the published quantum yields of anthracene ( $\phi_f$ =0.33), bianthryl ( $\phi_f$ =0.42), and tri(9,10-anthrylene) ( $\phi_f$ =0.60) in alkane solvents are considerably higher.<sup>[34]</sup> We tentatively attribute these differences to the fact that the DBA core in **5**, **9**, and **10** is a strong electron acceptor, thereby favoring TICT processes in comparison to the all-carbon systems, which, in turn, result in fluorescence quenching.

#### Conclusion

Five 9,10-dianthryl-9,10-dihydro-9,10-diboraanthracenes have been synthesized, fully characterized, and found to be stable toward air and moisture for extended periods of time. Each of these derivatives carries four *tert*-butyl groups on its anthryl substituents. Initially, we assumed that an ideal molecular design requires all four solubilizing substituents to be outward pointing. However, it turned out that the molecular framework is compatible even with four inward-point-

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ing *tert*-butyl groups and that their overall interactions seem to be attractive rather than repulsive. The latter substitution pattern is therefore particularly interesting, because the *tert*-butyl groups serve two purposes: 1) they increase the solubility of the molecule and 2) they provide additional steric shielding for the boron atoms. We also succeeded in the introduction of phenyl, dimesitylboryl, and *N*,*N*-di(*p*-tolyl)-amino groups into the anthryl substituents, which offer a handle to influence the optoelectronic properties of the molecules.

The UV/Vis absorption spectra of all five derivatives are characterized by broad charge-transfer bands in the range  $\lambda_{max}$ =510–556 nm; the corresponding fluorescence bands show strong positive solvatochromism. Four of the five 9,10-dianthryl-DBAs have been investigated by X-ray crystallog-raphy; all of them reveal twisted conformations about the exocyclic B–C bonds with dihedral angles ranging between 70° and 90°. We therefore conclude that the electronic spectra of our compounds are dominated by TICT interactions between the anthryl donors and the DBA acceptor. As a decisive difference, the all-carbon analogues, tri(9,10-anthrylene)s, feature three essentially identical subunits, none of them possessing distinct electron-donor or -acceptor properties.

The pronouncedly three-dimensional structures, the bulky *tert*-butyl groups, and the large Stokes shifts of our 9,10-dianthryl-DBAs help to suppress  $\pi$ - $\pi$  interactions and selfquenching in the solid state. As a result, bright fluorescence is observed for solid samples and we therefore suggest that the class of compounds presented herein is particularly promising for solid-state applications.

### **Experimental Section**

Unless otherwise specified, all reactions were carried out under dry nitrogen or argon with carefully dried and degassed solvents, flame-dried glassware, and Schlenk or glovebox techniques. Pentane, hexane, toluene, C6D6, and Et2O were dried over Na/benzophenone; CHCl3 was dried over CaH2 and freshly distilled prior to use; CDCl3 was dried over molecular sieves (4 Å). Solvents used for UV/Vis spectroscopic measurements were purchased as spectroscopic grade, dried over Na/K alloy (cyclohexane, C<sub>6</sub>H<sub>6</sub>, THF) or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>), and degassed prior to use. Column chromatography was performed by using silica gel 60 (Macherey-Nagel). NMR spectra were recorded with Bruker Avance 300 or Avance 400 spectrometers at room temperature. Chemical shifts are referenced to (residual) solvent signals ( ${}^{1}H/{}^{13}C{}^{1}H$ ); C<sub>6</sub>D<sub>6</sub>:  $\delta = 7.15/128.0$  ppm; CDCl<sub>3</sub>:  $\delta = 7.26/77.0$  ppm) or external BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B, <sup>11</sup>B{<sup>1</sup>H}). Abbreviations: s = singlet, d=doublet, dd=doublet of doublets, t=triplet, m=multiplet, br.=broad, app.=apparent, n.r.=multiplet not resolved, n.o.=signal not observed, i = ipso, o = ortho, m = meta, p = para. Electrochemical measurements were performed at room temperature by using an EG&G Princeton Applied Research 263A potentiostat with a platinum disk working electrode (diameter 2.00 mm). The reference electrode was a silver wire on which AgCl had been deposited by immersing the wire into HCl/HNO<sub>3</sub> (3:1). The solvent (THF) was dried over sodium without added benzoquinone at room temperature and degassed by five freezepump-thaw cycles. [nBu<sub>4</sub>N][PF<sub>6</sub>] (0.1 M) was employed as the supporting electrolyte. All potential values are referenced against the FcH/FcH+ couple ( $E_{1/2} = 0$  V). UV/Vis absorption and emission spectra were recorded with a Varian Cary 50 Scan UV/Vis spectrophotometer or a Spectrofluorometer FP-8300 (Jasco), respectively. The absolute fluorescence quantum yields ( $\phi_t$ ) were determined by using a calibrated integrating sphere system (ILF-835 100 mm diameter Integrating Sphere; Jasco), a quantum yield calculation program (FWQE-880; Jasco), and highly diluted samples of five different optical densities in each measurement. Mass spectra were recorded with a VG PLATFORM II mass spectrometer or a Fisons Instruments VG TofSpec mass spectrometer. Combustion analyses were performed by the Microanalytical Laboratory of the Goethe-University Frankfurt and by the Microanalytical Laboratory Pascher (Remagen, Germany).

General procedure for the synthesis of DBA derivatives 4/4', 5, 9, 10, and 11: *n*BuLi in hexane (3 equiv) was diluted with a threefold volume of hexane and added dropwise with stirring at -78 °C to a solution of the respective bromoanthracene (2 equiv) in Et<sub>2</sub>O. Stirring was continued for 15 min before the reaction mixture was warmed to room temperature within 1 h. The resulting turbid solution was cooled to -78 °C again, a solution of 3 (1 equiv) in toluene was added dropwise with stirring, the reaction mixture was eremoved under reduced pressure.

Synthesis of 4/4': Following the general procedure, 4/4' were synthesized from nBuLi (1.4 m in hexane, 1.4 mL, 1.9 mmol), 1 (465 mg, 1.26 mmol), and 3 (200 mg, 0.599 mmol); solvents were Et<sub>2</sub>O (40 mL) and toluene (25 mL). The crude product was washed with nondried MeOH (3  $\times$ 30 mL) and nondried pentane (3×30 mL) and further purified by flash column chromatography (silica gel 60). A mixture of nondried hexane and CHCl<sub>3</sub> (10:1) was employed as the mobile phase until all fractions showing blue fluorescence had been eluted from the column. Afterwards the polarity of the mobile phase was increased (hexane/CHCl<sub>2</sub>=2:1) to obtain 4/4' as a red solid (253 mg, 56 %). Both in solution and in the solid state, 4/4' show an intense red fluorescence when irradiated with UV light ( $\lambda_{ex}$  = 366 nm). Single crystals of 4 were grown by gas-phase diffusion of hexane into a concentrated solution of 4 in THF.  $R_f = 0.10$  (silica gel, hexane/CHCl<sub>3</sub>=5:1); <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =1.20 (s, 18H; C(CH<sub>3</sub>)<sub>3</sub>'), 1.26 (s, 18H; C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (s, 18H; C(CH<sub>3</sub>)<sub>3</sub>), 1.39 (s, 18H;  $C(CH_3)_3'$ ), 6.76 (m, 8H; H-b,b'), 7.22 (dd,  ${}^{3}J(H,H) = 9.0, {}^{4}J(H,H) = 2.0$  Hz, 2H; H-3), 7.36 (dd,  ${}^{3}J(H,H) = 9.0$ ,  ${}^{4}J(H,H) = 2.0$  Hz, 2H; H-3'), 7.53 (dd,  ${}^{3}J(H,H) = 9.0, {}^{4}J(H,H) = 2.0 \text{ Hz}, 2 \text{ H}; \text{ H-7'}), 7.57 \text{ (dd, } {}^{3}J(H,H) = 9.0, {}^{4}J\text{-}$  $(H,H) = 2.0 \text{ Hz}, 2H; H-7), 7.63 (m, 8H; H-a,a'), 7.97 (d, {}^{3}J(H,H) =$ 9.0 Hz, 2H; H-4), 8.04 (m, 6H; H-5,5',4'), 8.09 (m, 6H; H-8',1',1), 8.13 (d,  ${}^{3}J(H,H) = 9.0 \text{ Hz}, 2 \text{ H}; \text{ H-8}), 8.49 \text{ (s, } 2 \text{ H}; \text{ H-9'}), 8.50 \text{ ppm} \text{ (s, } 2 \text{ H}; \text{ H-9});$ <sup>11</sup>B NMR (96.3 MHz,  $C_6D_6$ ):  $\delta = n.o.$ ; <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $C_6D_6$ ):  $\delta = 30.9, 31.0, 31.1, 31.1$  (C(CH<sub>3</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>'), 4×35.0 (C(CH<sub>3</sub>)<sub>3</sub>, C-(CH<sub>3</sub>)<sub>3</sub>'), 123.5 (C-1), 123.6 (C-1'), 124.5 (C-3'), 124.6 (C-3), 124.9, 125.0, 125.0, 125.1 (C-5,5',7,7'), 126.3 (C-9,9'), 2×129.0 (C-8,8'), 130.0 (C-4'), 130.2 (C-4), 130.7 (C-8a), 130.8 (C-8a'), 2×132.0 (C-10a,10a'), 133.2 (C-4a'), 133.4 (C-4a), 134.2 (C-b'), 134.4 (C-b), 134.5 (C-9a'), 134.7 (C-9a), 140.5 (C-a'), 140.9 (C-a), 2×141.9 (C-10,10'), 146.5 (BC, BC'), 146.7 (C-6), 146.9 (C-6'), 147.2 (C-2'), 147.3 ppm (C-2); UV/Vis (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 367 (20800), 510 nm (1300 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); fluorescence (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{ex}$  = 366 nm,  $\lambda_{em} = 615$  nm; MS (MALDI): m/z (%): 753 (100) [ $M^+$ ]; elemental analysis calcd (%) for  $C_{56}H_{58}B_2$  (752.64)  $\times 0.2\,C_4H_8O$  (72.11): C 88.93, H 7.83; found: C 88.58, H 7.81 (the relative amount of  $C_4H_8O$  present in the sample was confirmed by <sup>1</sup>H NMR spectroscopy).

Synthesis of 5: Following the general procedure, 5 was synthesized from *n*BuLi (1.4 M in hexane, 1.8 mL, 2.5 mmol), 2 (600 mg, 1.62 mmol), and 3 (270 mg, 0.809 mmol); solvents were Et<sub>2</sub>O (40 mL) and toluene (25 mL). The crude product was washed with nondried MeOH (3×30 mL) and nondried pentane (3×30 mL) and further purified by flash column chromatography (silica gel 60; hexane/CHCl<sub>3</sub>=5:1) to obtain **5** as a red solid (525 mg, 86 %). Both in solution and in the solid state, **5** shows an intense red fluorescence when irradiated with UV light ( $\lambda_{ex}$ =366 nm). Single crystals of **5** were grown by gas-phase diffusion of hexane into a concentrated solution of **5** in C<sub>6</sub>H<sub>6</sub>. *R*<sub>f</sub>=0.14 (silica gel, hexane/CHCl<sub>3</sub>=5:1); <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =1.24 (s, 36H; C(CH<sub>3</sub>)<sub>3</sub>), 6.72 (m, 4H; H-b), 7.54 (dd, <sup>3</sup>*J*(H,H)=9.0, <sup>4</sup>*J*(H,H)=1.8 Hz, 4H; H-3,6), 7.62 (m, 4H; H-a), 8.02 (n.r., 4H; H-1.8), 8.10 (d, <sup>3</sup>*J*(H,H)=9.0 Hz, 4H; H-4.5), 8.51 ppm (s, 2H; H-10); <sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =73 ppm ( $h_{\mu}$ =3500 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =31.2 (C(CH<sub>3</sub>)<sub>3</sub>), 35.0 (C(CH<sub>3</sub>)<sub>3</sub>),

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124.7 (C-3,6), 125.1 (C-1,8), 126.1 (C-10), 129.1 (C-4,5), 130.5 (C-4a,10a), 134.1 (C-b), 135.3 (C-8a,9a), 140.9 (C-a), 142.0 (C-9), 146.4 (BC), 146.9 ppm (C-2,7); UV/Vis (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{max}$  ( $\varepsilon$ )=366 (15500), 510 nm (1050 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); fluorescence (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{ex}$ =366 nm,  $\lambda_{em}$ =610 nm; MS (MALDI): m/z (%): 753 (100) [ $M^+$ ]; elemental analysis calcd (%) for C<sub>56</sub>H<sub>58</sub>B<sub>2</sub> (752.64)×0.05 CHCl<sub>3</sub> (119.38): C 88.74, H 7.71; found: C 88.49, H 7.76 (the relative amount of CHCl<sub>3</sub> present in the sample was confirmed by <sup>1</sup>H NMR spectroscopy).

Synthesis of 9: Following the general procedure, 9 was synthesized from nBuLi (2.2м in hexane, 1.5 mL, 3.3 mmol), 6 (1000 mg, 2.245 mmol), and **3** (370 mg, 1.11 mmol); solvents were  $Et_2O$  (40 mL) and toluene (25 mL). The crude product was washed with nondried MeOH (3×30 mL) and nondried pentane ( $3 \times 30$  mL) and further purified by flash column chromatography (silica gel 60). A mixture of nondried hexane and CHCl<sub>3</sub> (10:1) was employed as the mobile phase until all fractions showing blue fluorescence had been eluted from the column. Afterwards the polarity of the mobile phase was increased (hexane/CHCl<sub>3</sub>=2:1) to obtain 9 as a red solid (857 mg, 85%). Both in solution and in the solid state, 9 shows an intense red fluorescence when irradiated with UV light ( $\lambda_{ex} = 366$  nm). Single crystals of 9 suitable for X-ray diffraction were obtained by gasphase diffusion of hexane into a concentrated solution of 9 in CH<sub>2</sub>Cl<sub>2</sub>.  $R_{\rm f} = 0.42$  (silica gel, hexane/CHCl<sub>3</sub>=3:1); <sup>1</sup>H NMR (300.0 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.23$  (s, 36 H; C(CH<sub>3</sub>)<sub>3</sub>), 6.87 (m, 4 H; H-b), 7.31 (dd, <sup>3</sup>J(H,H) = 9.0, <sup>4</sup>J- $(H,H) = 1.5 \text{ Hz}, 4H; H-3,6), 7.38 (t, {}^{3}J(H,H) = 7.3 \text{ Hz}, 2H; p-H), 7.50$ (app. t,  ${}^{3}J(H,H) = 7.3$  Hz, 4H; m-H), 7.79 (m, 4H; H-a), 7.82 (d,  ${}^{3}J$ - $(H,H) = 7.3 \text{ Hz}, 4H; o-H), 8.10 (d, {}^{3}J(H,H) = 9.0 \text{ Hz}, 4H; H-4,5),$ 8.15 ppm (d,  ${}^{4}J(H,H) = 1.5$  Hz, 4H; H-1,8);  ${}^{11}B$  NMR (96.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = \text{n.o.}; {}^{13}\text{C}{}^{1}\text{H} \text{NMR}$  (75.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 30.9$  (C(CH<sub>3</sub>)<sub>3</sub>), 35.2 (C-(CH<sub>3</sub>)<sub>3</sub>), 122.1 (C-1,8), 124.3 (C-3,6), 128.6 (p-C), 128.8 (m-C), 130.6 (C-4,5,8a,9a), 132.0 (o-C), 132.7 (C-4a,10a), 134.6 (C-b), 137.1 (C-9), 140.5 (i-C), 141.1 (C-a), 141.9 (C-10), 146.8 (BC), 147.7 ppm (C-2,7); UV/Vis (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 374 (28200), 531 nm (1500 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); fluorescence (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{ex}$  = 374 nm,  $\lambda_{em}$  = 635 nm; MS (MALDI): *m*/*z* (%): 905 (100)  $[M^+]$ ; elemental analysis calcd (%) for  $C_{68}H_{66}B_2$  (904.87)× 0.1 CHCl<sub>3</sub> (119.38): C 89.21, H 7.27; found: C 89.31, H 7.32 (the relative amount of CHCl3 present in the sample was confirmed by <sup>1</sup>H NMR spectroscopy).

Synthesis of 10: Following the general procedure, 10 was synthesized from nBuLi (2.8 m in hexane, 0.44 mL, 1.2 mmol), 7 (510 mg, 0.826 mmol), and 3 (138 mg, 0.414 mmol); solvents were Et<sub>2</sub>O (40 mL) and toluene (25 mL). The crude product was washed with nondried MeOH (3×30 mL) and nondried pentane (3×30 mL), redissolved in dry  $C_6H_6$ , and precipitated into pentane to obtain 10 as a red solid (423 mg, 82%). Both in solution and in the solid state, 10 shows an intense red fluorescence when irradiated with UV light ( $\lambda_{ex}$ =366 nm). Single crystals of 10 were grown by slow evaporation of a concentrated solution of 10 in THF under inert conditions. <sup>1</sup>H NMR (400.1 MHz,  $C_6D_6$ ):  $\delta = 1.16$  (s, 36H; C(CH<sub>3</sub>)<sub>3</sub>), 2.08 (s, 12H; *o*-CH<sub>3</sub>), 2.18 (s, 12H; *p*-CH<sub>3</sub>), 2.49 (s, 12H; o-CH<sub>3</sub>), 6.70 (brs, 4H; m-H), 6.93 (br.s, 4H; m-H), 6.96 (m, 4H; H-b), 7.21 (dd,  ${}^{3}J(H,H) = 8.9$ ,  ${}^{4}J(H,H) = 1.5$  Hz, 4H; H-3,6), 7.89 (m, 4H; H-a), 8.08 (d,  ${}^{3}J(H,H) = 8.9$  Hz, 4H; H-4,5), 8.55 ppm (d,  ${}^{4}J(H,H) = 1.5$  Hz, 4H; H-1,8); <sup>11</sup>B NMR (96.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = n.o.$ ; <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz,  $C_6D_6$ ):  $\delta = 21.3$  (p-CH<sub>3</sub>), 24.1, 24.2 (o-CH<sub>3</sub>), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>), 35.3 (C-CH<sub>3</sub>)) (CH<sub>3</sub>)<sub>3</sub>), 124.0 (C-3,6), 124.8 (C-1,8), 129.5, 129.7 (m-C), 130.9 (C-4,5), 132.7 (C-4a,10a), 134.6 (C-b), 134.7 (C-8a,9a), 139.7 (p-C), 140.6 (o-C), 140.9 (C-a), 141.4 (o-C), 145.5, 145.5 (C-9, C-10), 146.5 (BC), 146.8 (i-C), 147.4 ppm (C-2,7); UV/Vis (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{max}$  ( $\epsilon$ )=346 (17400), 442 (18300), 536 nm (2000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); fluorescence (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{ex} = 442$  nm,  $\lambda_{em} =$ 644 nm; MS (MALDI): m/z (%): 1249 (100) [M<sup>+</sup>]; elemental analysis calcd (%) for C<sub>92</sub>H<sub>100</sub>B<sub>4</sub> (1248.96): C 88.47, H 8.07; found: C 87.75, H 8.10.

**Synthesis of 11:** Following the general procedure, **11** was synthesized from *n*BuLi (1.5 M in hexane, 1.8 mL, 2.7 mmol), **8** (1000 mg, 1.771 mmol), and **3** (295 mg, 0.884 mmol); solvents were Et<sub>2</sub>O (50 mL) and toluene (20 mL). The crude product was washed with nondried MeOH ( $3 \times 30 \text{ mL}$ ), nondried CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 30 \text{ mL}$ ), and nondried pentane ( $3 \times 30 \text{ mL}$ ) to obtain pure **11** as a dark solid (563 mg, 56%). In the solid state, but not in solution, **11** shows an intense wine-red fluorescence

when irradiated with UV light ( $\lambda_{ex}$  = 366 nm). <sup>1</sup>H NMR (400.1 MHz,  $C_6D_6$ ):  $\delta = 1.23$  (s, 36H; C(CH<sub>3</sub>)<sub>3</sub>), 2.08 (s, 12H; *p*-CH<sub>3</sub>), 6.91 (m, 12H; *m*-H, H-b), 7.28 (dd,  ${}^{3}J(H,H) = 9.0$ ,  ${}^{4}J(H,H) = 1.8$  Hz, 4H; H-3,6), 7.43 (d,  ${}^{3}J(H,H) = 8.5 \text{ Hz}, 8 \text{ H}; o-\text{H}), 7.86 \text{ (m, 4H; H-a)}, 8.11 \text{ (d, }{}^{3}J(H,H) = 9.0 \text{ Hz},$ 4H; H-4,5), 8.69 ppm (d,  ${}^{4}J(H,H) = 1.8$  Hz, 4H; H-1,8);  ${}^{11}B$  NMR (96.3 MHz,  $C_6D_6$ ):  $\delta = n.o.$ ; <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $C_6D_6$ ):  $\delta = 20.7$  (*p*-CH<sub>3</sub>), 31.0 (C(CH<sub>3</sub>)<sub>3</sub>), 35.3 (C(CH<sub>3</sub>)<sub>3</sub>), 120.2 (C-1,8), 121.3 (o-C), 124.6 (C-3,6), 2×130.4 (m-C, p-C), 130.8 (C-8a,9a), 131.0 (C-4,5), 134.1 (C-4a,10a), 134.7 (C-b), 138.6 (C-9), 141.2 (C-a)\*, 142.0 (C-10)\*, 146.7 (BC), 147.2 (*i*-C), 148.9 ppm (C-2,7); UV/Vis (C<sub>6</sub>H<sub>6</sub>):  $\lambda_{max}$  ( $\epsilon$ ) = 359 (20300), 429 (14300), 556 nm (2200 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); fluorescence (solid state):  $\lambda_{ex} =$ 593 nm,  $\lambda_{em} = 675$  nm; MS (MALDI): m/z (%): 1143 (100) [M<sup>+</sup>]; elemental analysis calcd (%) for  $C_{84}H_{84}B_2N_2$  (1143.20)×0.3 CH<sub>2</sub>Cl<sub>2</sub> (84.93): C 86.64, H 7.30, N 2.40; found: C 86.38, H 7.32, N 2.23 (the relative amount of CH<sub>2</sub>Cl<sub>2</sub> present in the sample was confirmed by <sup>1</sup>H NMR spectroscopy). \*This signal was broadened beyond detection in the  $^{13}C{^1H}$  NMR spectrum; its chemical shift value was determined by using the cross peak in the HSQC or HMBC spectrum.

**Crystal structure analyses:** All crystals (except **6**, which was measured on a Siemens CCD three-circle diffractometer) were measured on a STOE IPDS-II diffractometer with graphite-monochromated  $Mo_{K\alpha}$  radiation. An empirical absorption correction with program PLATON<sup>[46]</sup> was performed for **1**, **2**, and **6–9**. The structures were solved by direct methods<sup>[47]</sup> and refined with full-matrix least-squares on  $F^2$  with the program SHELXL97.<sup>[48]</sup> H atoms were placed on ideal positions and refined with fixed isotropic displacement parameters by using a riding model.

In 2,7-DTBA, a hexane molecule is disordered over two positions with equal occupancies. The disordered atoms were isotropically refined; the C–C bond lengths were restrained to 1.50(1) Å and the *C*-C-*C* distances to 2.50(1) Å.

The molecule of  $\mathbf{1}$  is located on a crystallographic center of inversion. As a result, the Br atom and the H atom in the *para* position are mutually disordered with equal occupancies.

The absolute structure of **2** has been determined: Flack x parameter -0.006(9).

The crystal of **5** was a nonmerohedral twin with three domains (fractional contributions for the minor domains: 0.167(4) and 0.176(5)). The atoms of the solvent  $C_6H_6$  were isotropically refined. Equivalent C–C bond lengths and C-C-C bond angles were restrained to be equal.

In 6, one *tert*-butyl group is disordered over two positions with a site occupation factor of 0.643(8) for the major occupied site.

In 9, two *tert*-butyl groups are disordered over two positions with site occupation factors of 0.751(6) and 0.640(6) for the major occupied sites. These disordered atoms were isotropically refined. One CH<sub>2</sub>Cl<sub>2</sub> molecule, which was anisotropically refined, is disordered about a center of inversion with equal occupancies. Due to the absence of anomalous scatterers in 9, the absolute structure could not be determined and Friedel pairs were merged.

The crystal of 10 was very weakly diffracting and the atoms B(2), C(10), and C(12) were restrained to an isotropic behavior.

CCDC-887748 (4), CCDC-887749 (5), CCDC-887750 (9), CCDC-887751 (10), CCDC-887752 (1), CCDC-887753 (2), CCDC-887754 (6), CCDC-887755 (7), CCDC-887756 (8), CCDC-887757 (2,6-DTBA), CCDC-887758 (2,7-DTBA), CCDC-887759 (9-Ph-2,7-DTBA), CCDC-887760 (9-Mes<sub>2</sub>B-2,7-DTBA), and CCDC-887761 (9-Tol<sub>2</sub>N-2,7-DTBA) 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.

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