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Simultaneous expansion of 9,10 boron-doped anthracene in longitudinal and lateral directions†

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Doubly boron-doped anthracenes and pentacenes have been longitudinally and laterally expanded through annulation of thiophene or benzene rings. The obtained series of closely related compounds allowed an assessment of key structure-property relationships with a focus on optoelectronic characteristics. Most of the products are benchtop-stable blue emitters and capable of accepting two electrons in a reversible manner. The syntheses involved late-stage modifications through photocyclization or stepwise oxidative C-C coupling (DDQ/BF₃·Et₂O) as well as cyclocondensation of *ortho*-disilylated or -diborylated aryl building blocks.

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Introduction

It is nowadays beyond discussion that the development of novel materials benefits greatly if "inorganic" p-block elements are combined with carbon-based matrices.¹ In the specific area of organic electronics, boron has been established as a particularly valuable dopant of the ubiquitous polycyclic aromatic hydrocarbons (PAHs). Applications of B-containing PAHs (B-PAHs) range from metal-free catalysis²⁻⁴ and sensor technology⁵ to battery materials, organic field-effect transistors, and organic light-emitting devices.⁶ Among the currently available B-PAHs, the 9,10-dihydro-9,10-diboraanthracenes (DBAs) stand out for their vicinally positioned, cooperating B atoms.⁷⁻⁹ Three expedient synthesis routes are available for the assembly of the DBA scaffold: (i) cyclocondensation of 1,2-(SiMe₃)₂-C₆H₄ with BBr₃,¹⁰⁻¹² (ii) cyclocondensation of $[1,2-(BH_3)_2-C_6H_4]^{2-}$ upon H⁻ abstraction with Me₃SiCl,^{13,14} (iii) cyclodimerization of 1-Li-2-B(OR)2-C6H4.15,16 Methods (i) and (iii) have also been employed for the synthesis of C-halogenated DBAs,^{12,15-18} which are viable starting materials for Stille-type coupling reactions to introduce a broad variety of dangling substituents (Chart 1).^{12,16,19,20}

Additional protocols exist for the longitudinal^{21–24} or lateral^{20,25} expansion of the DBA lead structure (Chart 1). Herein we report on the synthesis, structural, and opto-

†Electronic supplementary information (ESI) available. CCDC 1883314-1883317 and 1883327-1883336. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04820g electronic properties of longitudinally *and* laterally expanded DBAs, the all-carbon congeners of which have recently been advertised as candidate materials for single-crystal field-effect transistor (SCFET) devices.²⁶



Chart 1 Benchtop-stable 9,10-dihydro-9,10-diboraanthracene (DBA; dashed frame) and representative derivatives of it obtained through peripheral substitution or longitudinal/lateral expansion (Mes = mesityl).

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Results and discussion

Synthesis of longitudinally tetrafused DBAs

Our synthesis of a 9,18-dibora-tetrabenz[a,c,h,j]anthracene (cf. 2; Scheme 1) is based on the 9,10-diborylated phenanthrene 1 bearing two solubilizing *tert*-butyl (*t*-Bu) groups. 1 is accessible from 1,2-bis(4-t-Bu-C₆H₄)acetylene and B₂pin₂ through a Cu-catalyzed diborylation reaction,²⁷ followed by photocyclization of the obtained (Z)-stilbene intermediate (cf. the ESI† for full details).²⁸ Conversion of 1 into the corresponding trihydridoborate using LiAlH₄ and subsequent hydride abstraction with Me₃SiCl in the solvent SMe₂ resulted in a cyclocondensation reaction¹³ to form the diadduct $2^{H} \cdot 2SMe_2$ together with BH₃·SMe₂ as the byproduct. We succeeded in the growth of single crystals of 2^H·2SMe₂, but failed to separate 2^H·2SMe₂ and BH₃·SMe₂ via fractional crystallization on a preparative scale. Attempts to quantitatively remove the BH₃·SMe₂ under a dynamic vacuum (10⁻³ mbar, rt, 4 h) were also in vain, however, NMR spectroscopy indicated the loss of both SMe₂ ligands from 2^H·2SMe₂. Similar to the SMe₂ diadduct of pristine DBA (DBA·2SMe₂),^{7,11,29,30} 2^H·2SMe₂ reacts with the alkynes *t*-Bu-C=CH and 4-*t*-Bu-C₆H₄C=CH already at room temperature. Contrary to the case of DBA·2SMe₂, no welldefined hydroboration products could be detected. The targeted hydrolysis of the 2^H·2SMe₂/BH₃·SMe₂ mixture gave the borinic acid derivative 2^{OH} of 9,18-dibora-tetrabenz[*a,c,h,j*]anthracene in single-crystalline form. An X-ray analysis (*cf.* the ESI†) of the colorless, non-fluorescent compound showed a distorted molecular scaffold already with the small OH substituent, which explains why the above-mentioned hydroboration reactions had not been straightforward. Likely also for steric reasons it proved impossible to synthesize the bromoborane 2^{Br} through the reaction of BBr₃ with either the borinic acid 2^{OH} or 9,10-(SiMe₃)₂-phenanthrene 3 (*cf.* the ESI† for more information about the inaccessibility of 3,6-(*t*-Bu)₂-3).^{12,16,31} Given that the lack of 2^{Br} renders corresponding B-arylated derivatives inaccessible, we moved on to the sterically less congested longitudinally expanded 6,13-dihydro-6,13-diborapentacenes (DBPs).

Synthesis of longitudinally tetrafused DBPs

Evidence that an annulation of four aryl rings to a DBP core is compatible even with sterically demanding mesityl (Mes) substituents at the B atoms was first obtained during repeated emission measurements on the same sample of the known¹² $4^{\rm H}$ (Scheme 2): small differences between the individual fluorescence spectra indicated a progressing photocyclization between vicinal thienyl substituents already in the weak UV beam of the spectrometer (*cf.* the related UV-photocyclization of 1,2-bis(2-thienyl)ethylenes³²). On an NMR scale, the tar-





Scheme 1 Synthesis of the tetrafused DBA 2^{H} (obtained as diadduct 2^{H} ·2SMe₂). Reagents and conditions: (i) LiAlH₄ (3.0 eq.), Et₂O, 0 °C, 14 h; (ii) Me₃SiCl (3.3 eq.), SMe₂, 60 °C, 4 d (sealed ampoule); (iii) CuBr₂ (10.0 eq.), EtOAc/MeOH/H₂O, 130 °C, 4 h; (iv) Mg (4.0 eq.), 1,2-Br₂C₂H₄ (0.2 eq.), Me₃SiCl (8.0 eq.), THF, reflux temperature, 18 h; (v) BBr₃ (3.5 eq.), *n*-hexane, 120 °C, 3 d (sealed ampoule).

Scheme 2 Synthesis of singly (5) and doubly (6) ring-closed derivates of 4 *via* photocyclization (6^{H} , 6^{Me}) and oxidative cyclization reactions (5^{Me} , 6^{Me}). Reagents and conditions: (i) Irradiation with a medium pressure Hg lamp (NMR scale), C_6D_6 , rt, 6 h; (ii) DDQ (1.1 eq.), BF₃·Et₂O (10 eq.), CH₂Cl₂, rt, 4.5 h; (iii) DDQ (2 eq.), BF₃·Et₂O (10 eq.), CH₂Cl₂, 50 °C, 16 h; (iv) DDQ (4 eq.), BF₃·Et₂O (20 eq.), CH₂Cl₂, 50 °C, 41 h.

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geted photoreaction of 4^{H} in non-dried, non-degassed C_6D_6 using a medium pressure Hg lamp furnished no singly cyclized 5^{H} but exclusively the DBP derivative 6^{H} (quantitative conversion, 56% yield; Scheme 2). However, 6^H turned out to be photolabile, which precluded its photochemical synthesis on larger scales. This situation did not change with the DBA 4^{Me} as starting material (Scheme 2), even though its four reactive thienyl α -positions are blocked with methyl groups – a strategy successfully applied in comparable cases.²³ Scholl-type oxidative protocols are viable alternatives to photocyclization reactions.³³ In the case of 4^{Me}, the combination of 2,3dichloro-5,6-dicvano-1,4-benzoquinone (DDQ) and BF3·Et2O performed best and provided selective access not only to the doubly ring-closed derivative 6^{Me} (DDO (4.0 eq.), BF₃·Et₂O (20 eq.), 50 °C, 41 h), but also to the singly ring-closed diboratetracene 5^{Me} (DDQ (1.1 eq.), BF₃·Et₂O (10 eq.), rt, 4.5 h; Scheme 2).

To prepare the true laterally expanded homolog of the DBA 2 and to evaluate the influence of the four S atoms on the optoelectronic properties of 6-type PAHs, we next aimed at the quadruply benzannulated DBP 8 (Scheme 3). To this end, the tetraphenylated DBA 7 was prepared from 2,3,6,7-Cl₄-9,10-Mes₂-DBA and 1-SnMe₃-3-*t*-Bu-C₆H₄ *via* a Stille coupling reaction (*cf.*, ref. 12). Different from its thienyl congener, however, 7 neither underwent photocyclization nor oxidative C–C coupling with DDQ/BF₃-Et₂O. We therefore had to come back to the



NMR spectroscopy

NMR spectra $({}^{1}H, {}^{11}B_{1}{}^{1}H\}$, and ${}^{13}C_{1}{}^{1}H\}$) were recorded in CDCl₃. As often encountered for triarylboranes, ¹¹B signals were generally broadened beyond detection.³⁶ For each of the reported B-doped PAHs, the numbers and chemical shift values of its ¹H and ¹³C resonances agreed with the proposed molecular structure. Diagnostic for a successful cyclization,^{21,23} the signals of protons pointing into the newly formed bay regions experience significant downfield shifts (e.g. 4^{Me}: 6.59 ppm vs. 6^{Me}: 7.30 ppm; see also: 7: 7.19 ppm vs. 8: 8.51 ppm). The chemical shift differences between the p- and o-CH₃ proton signals in Mes-substituted cyclic conjugated π systems provide a measure of the overall magnetic anisotropy, which strongly correlates with the ring current $[\Delta \delta = \delta(p-CH_3)]$ $-\delta(o-CH_3)$].³⁷ This approach yields the same qualitative results as quantum-chemical calculations.³⁸ 9,10-Mes₂-anthracene and 9,10-Mes₂-DBA have $\Delta\delta$ values of 0.70 (ref. 39) and 0.33,²⁵ respectively, which indicate a larger ring current on the central part of the anthracene fragment than on the B_2C_4 heterocycle and, in turn, a limited degree of B=C double-bond character. A $\Delta\delta$ value of 0.37 measured for 6,13-Mes₂-DBP²⁵ points toward a slightly increased π delocalization across the B centers. This can be explained by the fact that, in DBA, both B-attached benzene rings contain Clar's sextets, whereas in DBP the two sextets can alternatively be assigned to the peripheral benzene rings. Similar arguments are applicable to the DBP 8, the $\Delta\delta$ value of which is smaller by 0.13 than that of 6,13-Mes₂-DBP: if Clar's sextets are drawn in all t-Bu-substituted cycles of 8, one necessarily has to draw them also in the B-attached benzene rings, which renders 8 more comparable to DBAs than DBPs. More experimental evidence for a diminished aryl-to-B π -electron donation in 8 stems from cyclic voltammetry (vide infra), which shows 8 to be a better electron acceptor ($E_{1/2} = -1.82$ V) than 6,13-Mes₂-DBP ($E_{1/2} = -2.03$ V).²⁵ Moreover, the $\Delta\delta$ values of 7 (0.11) vs. 8 (0.24) and 4^{Me} (0.24) vs. 5^{Me} (0.29) vs. 6^{Me} (0.35) indicate that the degree of π delocalization across the central B₂C₄-ring increases with an increasing extension of the organic π system.

Crystal structures

The molecular structures of $2^{H} \cdot 2SMe_2$, 2^{OH} (*cf.* the ESI[†]), 6^{H} , and 8 have been confirmed by X-ray crystallography. The adduct $2^{H} \cdot 2SMe_2$ contains an inversion center in the solid state (Fig. 1). Each tetracoordinated B atom deviates strongly from a tetrahedral configuration and approaches a trigonalpyramidal geometry with the SMe₂ ligand located at the apical position (sum of C–B–C/C–B–H angles = 350°; sum of C–B– S/H–B–S angles = 303°). The B–S bond length amounts to



Fig. 1 Molecular structures of tetrabenzanthracene (CCDC 1839293, ref. 26), $2^{H}\cdot 2SMe_2$, and 9,18-diphenyltetrabenzanthracene (CCDC 1151346, ref. 42) in the solid state (C atoms: black, H atoms: light grey, B atoms: green, S atoms: yellow). C-Bonded H atoms and t-Bu groups located at the C atoms marked with (*) are omitted for clarity. Selected bond lengths [Å], and angles [°] of $2^{H}\cdot 2SMe_2$: B-C = 1.600(3)/1.603(3), B-H = 1.10(2), B-S = 2.118(2); C-B-C = 118.94(18), H-B-S = 98(1), C-B-S = 98.1(1)/106.5(1), C-B-H = 116(1)/115(1).

2.118(2) Å. For comparison, DBA·2SMe₂ possesses an average sum of C-B-C/C-B-H angles of 342° and C-B-S/H-B-S angles of 314°. Especially the short average B-S bond length of 2.031 Å in DBA·2SMe₂ points toward a stronger adduct.⁷ The C-C distance within the central B₂C₄ ring of 2^H·2SMe₂ (1.379(3) Å) lies between the length of the localized phenanthrene C=C double bond (1.351 Å, average value of six crystal structures)⁴⁰ and that of the aromatic bond in tetrabenzanthracene (1.415(2) Å; Fig. 1).²⁶ Differences between 2^H·2SMe₂ and DBA·2SMe2 are also evident for the mutual orientations of the SMe₂ ligands, which coordinate in anti- and syn-fashions, respectively. The torsion angle spanned by the four C atoms in the bay region of $2^{H}\!\cdot\! 2SMe_2$ has an absolute value of 10.5(3)° and the gulf region⁴¹ is even less distorted $(1.7(2)^\circ)$. Compared to the parent tetrabenzanthracene (bay twist = $3.5(2)^\circ$, gulf twist = $1.6(1)^{\circ}$; Fig. 1),²⁶ 2^H·2SMe₂ deviates only slightly stronger from planarity. The presence of two phenyl rings at the center of the gulf region of tetrabenzanthracene results in a severe helical distortion (average bay twist = 15.6°, average gulf twist = 69.7° ; Fig. 1),⁴² which explains why we have not been able to replace the H atoms at the B sites of 2^H by Br, let alone Ph/Mes substituents.

The DBP **8** is formally derived from the DBA **2** through the introduction of benzenoid spacers. The thus expanded gulf regions can now host even bulky Mes substituents without significant distortion of the centrosymmetric molecular backbone (bay twist = $8.0(3)^\circ$, expanded gulf twist = $12.5(2)^\circ$, Mes//B₂C₄ = 70.6° ; Fig. 2). The main scaffold of the thieno-fused DBP **6**^H (point group C_i) is almost perfectly planar (bay twist = $0.9(8)^\circ$, expanded gulf twist = $5.2(2)^\circ$, Mes//B₂C₄ = 86.8° ; Fig. 2). In **8** as well as **6**^H, the exocyclic and averaged endocyclic B–C bonds are very much alike, which again underscores the small extent of π delocalization *via* the B centers in the electronic ground states (**8**: B–C_{exo} = 1.572(2) Å *vs*. B–C_{endo} = 1.566 Å; **6**^H: B–C_{exo} = 1.585(7) Å *vs*. B–C_{endo} = 1.565 Å).

Electrochemical and optoelectronic properties

Cyclic voltammograms (CVs) were recorded in THF with $[n-\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte and are referenced against the ferrocene/ferrocenium (FcH/FcH⁺) couple. The methylthieno-fused $\mathbf{6}^{\text{Me}}$ shows irreversible redox behavior with a cathodic peak potential of $E_{\text{pc}} = -1.94$ V. All other Mes-substituted compounds, including the non-methylated thieno-fused $\mathbf{6}^{\text{H}}$, show two reversible redox waves. The first half-wave potentials $E_{1/2}$ of 7 and the fully benzenoid 8 are identical (-1.82 V; Table 1). In the cases of the S-containing species, the $E_{1/2}$ values become slightly more cathodic upon successive cyclization: $\mathbf{4}^{\text{Me}}$ (-1.68 V) < $\mathbf{5}^{\text{Me}}$ (-1.78 V) < $\mathbf{6}^{\text{H}}$ (-1.83 V). The similar electron affinities of ring-opened and respective ring-closed B-PAHs are likely due to the fact that Clar's sextets can be drawn in all peripheral aryl rings, irrespective of whether they are directly connected or not. The second reduction



Fig. 2 Molecular structures of **8** and **6**^H in the solid state (C atoms: black, B atoms: green, S atoms: yellow). H atoms and the *t*-Bu groups located at the carbon atoms marked with (*) are omitted for clarity. Only the Mes-C-*i* atoms are shown for the Mes substituents. Selected bond lengths [Å] and angles [°]: **8**: $B-C_{endo} = 1.565(2)/1.566(2)$, $B-C_{exo} = 1.572(2)$; $C_{endo}-B-C_{endo} = 118.5(2)$, $C_{endo}-B-C_{exo} = 123.2(2)/118.2(2)$. **6**^H: $B-C_{endo} = 1.561(7)/1.569(6)$, $B-C_{exo} = 1.585(7)$; $C_{endo}-B-C_{endo} = 119.1(4)$, $C_{endo}-B-C_{exo} = 121.4(4)/119.3(4)$.

Table 1 Electrochemical and photophysical data for 4^{Me} , 5^{Me} , 6^{Me} , 6^{H} , 7, 8, and 6,13-Mes₂-DBP

			1	-	1	
Cmpd	$\Delta \delta^a$	$E_{1/2}^{b}$ [V]	$\lambda_{abs}^{c,a}$ [nm]	λ _{ex} [nm]	$\lambda_{em}^{c,a}$ [nm]	Φ_{PL} [%]
- Me			f			
-Me	0.24	-1.68	397 ⁷	397	538	19
		-2.47			- o - ^o	•
5	0.29	-1.78	451	360	507 ^s	20
		-2.48	427			
6 ^{Me}	0.35	_/	451	370	455	26
			425		485	
					514	
6 ^H	0.33	-1.83	440	359	444	24
		-2.47	415		472	
			392		503	
7	0.11	-1.82	371	304	483	8
		-2.73	304			
8	0.24	-1.82	430	350	438	56
		-2.44	405		463	
			385		495	
			350		150	
6.13-Mes -DBP ^h	0.37	-2.03	407	303	412	47
0,13-MC52-DBP	0.37	-2.03	206	303	412	47
		-2.75	300		454	
			329		461	
			303		491	

 ${}^{a}\Delta\delta = \delta(p\text{-CH}_{3}) - \delta(o\text{-CH}_{3}). {}^{b}\text{THF}, [n\text{-Bu}_{4}\text{N}][\text{PF}_{6}]$ (0.1 M). ${}^{c}\text{In cyclohexane.}^{d}$ Vibrational bands are also listed. ${}^{e}\text{Quantum yields}$ were determined from degassed samples by using a calibrated integrating sphere. ${}^{f}\text{Bathochromic shoulder at approx. 470 nm. }{}^{g}\text{Hypsochromic shoulder at approx. 455 nm.}^{h}\text{Values taken from ref. 25.}$

occurs at nearly the same electrode potential for any of the investigated diboraacene-derivatives (8: -2.44 V, 4^{Me} : -2.47 V, 5^{Me} : -2.48 V, 6^{H} : -2.47 V) with the exception of 7, for which the injection of a second electron is somewhat harder to achieve (-2.73 V). As mentioned above for Mes-substituted aryls, $\Delta \delta = \delta (p\text{-CH}_3) - \delta (o\text{-CH}_3)$ can be taken as a gauge to estimate the ring current within the aryl ring: a higher $\Delta \delta$ is associated with a larger ring current and, in the specific case of mesitylated B-PAHs, a higher π -electron density at the B centers. By these means, an increasing $\Delta \delta$ along a series of closely related B-PAHs should lead to a gradual cathodic shift of the reduction potentials $E_{1/2}$. This rule of thumb indeed holds for $4^{Me}/5^{Me}/6^{H}$ as well as 8/6,13-Mes₂-DBP (Table 1). Only the pair 7/8 is an outlier, because both compounds have identical redox potentials yet different $\Delta \delta$ values.

All B-PAHs discussed herein possess yellow to orange colors. Electronic spectra were recorded in cyclohexane solutions at room temperature. 4^{Me} with four dangling methyl-thienyl substituents shows a featureless absorption band at 397 nm with a bathochromic shoulder ($\lambda_{onset} = 495$ nm; Fig. 3a). For the pristine 9,10-Mes₂-DBA, which gives rise to a qualitatively similar UV/vis spectrum, it has been firmly established that the shoulder is due to an intramolecular charge transfer from the electron-rich Mes substituents to the electron-poor DBA core.^{16,43} A comparable methylthienyl-to-DBA transition likely takes place in the case of 4^{Me} . The emission band of 4^{Me} has a maximum at $\lambda_{em} = 538$ nm and is also very broad, due to rotation/libration of the methylthienyl substituents (Fig. 3b). The intramolecular motions also open an efficient non-radiative decay channel, which, together with the





Fig. 3 Absorption (a) and emission (b) spectra of the methylthienyl derivatives 4^{Me} , 5^{Me} , and 6^{Me} . All measurements were performed in cyclohexane.

charge-transfer nature of the transition, explains the low fluorescence quantum yield of $\Phi_{\rm PL}$ = 19%. The doubly ring-closed 6^{Me} possesses a longest-wavelength absorption at λ_{abs} = 451 nm with resolved vibrational fine structure; the corresponding emission band at λ_{em} = 455 nm is the perfect mirror image and $\Phi_{\rm PL}$ increases to a value of 26%. The absorption spectrum of the singly ring-closed 5^{Me} is similar to that of 6^{Me} (longest wavelength absorption: $\lambda_{abs} = 451$ nm), but the individual bands are somewhat broader. In contrast, the fluorescence spectrum of 5^{Me} resembles that of tetrathienylated 4^{Me}, apart from a hypsochromic shift of the emission band ($\lambda_{em} = 507$ nm, $\Phi_{\rm PL}$ = 20%). Thus, the absorption and emission spectra of 5^{Me} are not mirror images, which testifies to structural reorganizations taking place in the excited state. Analogous general features as in the case of 4^{Me} vs. 6^{Me} are also observable for 7 vs. 8 (Table 1; cf. the ESI[†] for plots of the spectra). As a distinct difference, the quantum efficiency increases from $\Phi_{\rm PL}$ = 8% to as much as 56% upon going from 7 to 8.

Conclusions

Despite its sterically encumbered gulf regions, tetrabenzanthracene is a planar molecule. Already the introduction of two

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phenyl rings at the central (9,18) positions results in a severe skeletal twist. Also the SMe₂ diadduct of a 9,18-boron-doped tetrabenzanthracene (2^H·2SMe₂) retains an essentially planar scaffold. The B-H functionalities can still be transformed into B-OH groups, whereas larger Br substituents are not compatible with the confined space surrounding the B atoms. The steric strain in the gulf regions can be alleviated by switching from a diboraanthracene to a diborapentacene backbone. The tetrabenzodiborapentacene 8 was prepared via cyclocondensation of an ortho-disilylated triphenylene with BBr3. While several attempts failed to obtain 8 also through photocvclization or intramolecular Scholl-type C-C coupling of the 2,3,6,7-tetraphenyl diboraanthracene 7, these methods faithfully worked for the synthesis of the tetrathienodiborapentacene 6^{Me} from 2,3,6,7-tetrathienyl diboraanthracene 4^{Me}. The Scholl protocol (DDQ/BF3·Et2O) is not only the method of choice to synthesize 6^{Me} on a preparative scale, but also allows a selective monocyclization of 4^{Me} to furnish the diboratetracene 5^{Me}. The electronic spectra of the tetraarvlated species 4^{Me} and 7 are characterized by broad absorption and emission bands with contributions from charge-transfer transitions between the dangling substituents and the B₂C₄ rings. In stark contrast, the fully planarized products 6^{Me} and 8 give rise to vibrationally resolved UV/vis and fluorescence spectra. Of particular interest is the partially planarized diboratetracene 5^{Me}, because its absorption spectrum resembles that of 6^{Me} , whereas its emission spectrum is qualitatively similar to that of 4^{Me}.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- 1 *Main Group Strategies Towards Functional Hybrid Materials*, ed. T. Baumgartner and F. Jäkle, John Wiley & Sons Ltd, Chichester, 2018.
- 2 F.-G. Fontaine and É. Rochette, Acc. Chem. Res., 2018, 51, 454-464.
- 3 E. von Grotthuss, A. John, T. Kaese and M. Wagner, *Asian J. Org. Chem.*, 2018, 7, 37–53.

- 4 L. Schweighauser and H. A. Wegner, *Chem. Eur. J.*, 2016, **22**, 14094–14103.
- 5 C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, *Chem. Rev.*, 2010, **110**, 3958–3984.
- 6 (a) Ref. 3; (b) L. Ji, S. Griesbeck and T. B. Marder, Chem. Sci., 2017, 8, 846–863; (c) A. Escande and M. J. Ingleson, Chem. Commun., 2015, 51, 6257–6274; (d) A. Wakamiya and S. Yamaguchi, Bull. Chem. Soc. Jpn., 2015, 88, 1357–1377; (e) A. Lorbach, A. Hübner and M. Wagner, Dalton Trans., 2012, 41, 6048–6063; (f) Z. M. Hudson and S. Wang, Dalton Trans., 2011, 40, 7805–7816.
- 7 A. Lorbach, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. Commun.*, 2010, **46**, 3592–3594.
- 8 A. Lorbach, M. Bolte, H.-W. Lerner and M. Wagner, Organometallics, 2010, 29, 5762–5765.
- 9 L. Schweighauser, I. Bodoky, S. N. Kessler, D. Häussinger, C. Donsbach and H. A. Wegner, *Org. Lett.*, 2016, 18, 1330– 1333.
- 10 W. Schacht and D. Kaufmann, J. Organomet. Chem., 1987, 331, 139–152.
- 11 E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H.-W. Lerner and M. Wagner, *Chem. – Eur. J.*, 2011, 17, 12696–12705.
- 12 C. Reus, S. Weidlich, M. Bolte, H.-W. Lerner and M. Wagner, J. Am. Chem. Soc., 2013, 135, 12892–12907.
- 13 Ö. Seven, Z.-W. Qu, H. Zhu, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Chem. – Eur. J.*, 2012, 18, 11284–11295.
- 14 Ö. Seven, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2014, **33**, 1291–1299.
- 15 S. Luliński, J. Smętek, K. Durka and J. Serwatowski, *Eur. J. Org. Chem.*, 2013, 8315–8322.
- 16 S. Brend'amour, J. Gilmer, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. – Eur. J.*, 2018, 24, 16910–16918.
- 17 A. Lorbach, C. Reus, M. Bolte, H.-W. Lerner and M. Wagner, *Adv. Synth. Catal.*, 2010, **352**, 3443–3449.
- 18 C. Reus, N.-W. Liu, M. Bolte, H.-W. Lerner and M. Wagner, J. Org. Chem., 2012, 77, 3518–3523.
- 19 C. Reus, F. Guo, A. John, M. Winhold, H.-W. Lerner, F. Jäkle and M. Wagner, *Macromolecules*, 2014, 47, 3727– 3735.
- 20 A. John, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2017, **56**, 5588–5592.
- 21 V. M. Hertz, M. Bolte, H.-W. Lerner and M. Wagner, *Angew. Chem., Int. Ed.*, 2015, **54**, 8800–8804.
- 22 V. M. Hertz, H.-W. Lerner and M. Wagner, Org. Lett., 2015, 17, 5240–5243.
- 23 V. M. Hertz, J. G. Massoth, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. – Eur. J.*, 2016, 22, 13181–13188.
- 24 V. M. Hertz, N. Ando, M. Hirai, M. Bolte, H.-W. Lerner, S. Yamaguchi and M. Wagner, *Organometallics*, 2017, 36, 2512–2519.
- 25 S. Kirschner, J.-M. Mewes, M. Bolte, H.-W. Lerner, A. Dreuw and M. Wagner, *Chem. – Eur. J.*, 2017, **23**, 5104–5116.
- 26 S. Kumar, D.-C. Huang, S. Venkateswarlu and Y.-T. Tao, *J. Org. Chem.*, 2018, **83**, 11614–11622.

- 27 H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita and K. Takaki, *Angew. Chem., Int. Ed.*, 2012, **51**, 235–238.
- 28 M. Shimizu, I. Nagao, Y. Tomioka, T. Kadowaki and T. Hiyama, *Tetrahedron*, 2011, 67, 8014–8026.
- 29 A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle and M. Wagner, *Angew. Chem.*, *Int. Ed.*, 2009, 48, 4584–4588.
- 30 E. Januszewski, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2012, **31**, 8420-8425.
- 31 E. R. Abbey, A. N. Lamm, A. W. Baggett, L. N. Zakharov and S.-Y. Liu, J. Am. Chem. Soc., 2013, 135, 12908–12913.
- 32 F. B. Mallory and C. W. Mallory, *Org. React.*, 1984, 30, 1–456.
- 33 (a) R. Scholl and C. Seer, *Eur. J. Org. Chem.*, 1912, 394, 111–177; (b) J. Wu, W. Pisula and K. Müllen, *Chem. Rev.*, 2007, 107, 718–747; (c) X. Feng, W. Pisula and K. Müllen, *Pure Appl. Chem.*, 2009, 81, 2203–2224; (d) L. Zhai, R. Shukla and R. Rathore, *Org. Lett.*, 2009, 11, 3474–3477; (e) D. Waghray, C. de Vet, K. Karypidou and W. Dehaen, *J. Org. Chem.*, 2013, 78, 11147–11154.
- 34 J. Chen, J. W. Kampf and A. J. Ashe III, *Organometallics*, 2008, 27, 3639–3641.
- 35 B. C. Berris, G. H. Hovakeemian, Y. H. Lai, H. Mestdagh and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1985, **107**, 5670– 5687.

- 36 H. Nöth and B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in *NMR Basic Principles* and Progress, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, 1978.
- 37 B. Bock, M. Kuhr and H. Musso, Chem. Ber., 1976, 109, 1184–1194.
- 38 A. Iida and S. Yamaguchi, J. Am. Chem. Soc., 2011, 133, 6952-6955.
- 39 Y. Yamamoto, K. Wakamatsu, T. Iwanaga, H. Sato and S. Toyota, *Chem. – Asian J.*, 2016, **11**, 1370–1375.
- 40 (a) J. Trotter, Acta Crystallogr., 1963, 16, 605–608;
 (b) D. W. Jones and J. Yerkess, J. Cryst. Mol. Struct., 1971, 1, 17–23;
 (c) M. I. Kay, Y. Okaya and D. E. Cox, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1971, 27, 26–33;
 (d) V. Petřiček, I. Cisařová, L. Hummel, J. Kroupa and B. Brězina, Acta Crystallogr., Sect. B: Struct. Sci., 1990, 46, 830–832;
 (e) F. P. A. Fabbiani, D. R. Allan, W. I. F. David, S. A. Moggach, S. Parsons and C. R. Pulham, CrystEngComm, 2004, 82, 504–511.
- 41 C. L. Hilton, J. M. Crowfoot, P. Rempala and B. T. King, J. Am. Chem. Soc., 2008, **130**, 13392–13399.
- 42 R. A. Pascal, W. D. McMillan and D. Van Engen, J. Am. Chem. Soc., 1986, **108**, 5652–5653.
- 43 C. Hoffend, M. Diefenbach, E. Januszewski, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Dalton Trans.*, 2013, 42, 13826–13837.